

**PRODUCTION OF BUTYL GLUCOSIDES by  
Zr-SBA-15 & SO<sub>4</sub>/Zr-SBA-15 CATALYSTS**

**A Thesis Submitted to  
the Graduate School of Engineering and Sciences of  
İzmir Institute of Technology  
in Partial Fulfillment of the Requirements for the Degree of  
MASTER OF SCIENCE  
in Chemical Engineering**

**by  
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**July 2020  
İZMİR**

## ACKNOWLEDGEMENTS

I would like to thank my supervisor Prof. Dr. Selahattin Yılmaz for his great contributions, support and encouragements in the preparation of this thesis.

I am grateful to Vahide Nuran Mutlu for her great help and guidance during my experimental study.

I would like to thank to my committee members Assoc. Prof. Dr. Meral Dkkanc and Assist. Prof. Dr. Bařar aęlar for their valuable suggestions and recommendations to improve the quality of my thesis.

I am thankful to Research Specialists Filiz Kurucaoval, Nesrin Ahpařaoęlu, zlem aęlar Duvarc and Deniz Őimřek for their understanding and helping for the analysis during my experimental study.

I would like to thank my dear friends Yařar Kemal Receptoęlu, Azime Arıkaya, Alphan Berkem, Ceren Orak, Devran Demirbař, Berem Hanoęlu and Cansu nercan for their good fellowship.

I thank my parents and my brother for always giving me inspiration and strength even in my most difficult times.

This study was supported financially by The Scientific and Technological Research Council of Turkey (TUBITAK). Project Number is 117M160. Their support is gratefully acknowledged.

## ABSTRACT

### PRODUCTION OF BUTYL GLUCOSIDES by Zr-SBA-15 & SO<sub>4</sub>/Zr-SBA-15 CATALYSTS

The purpose of this study was to develop mesoporous solid acid catalyst for glycosidation reaction of butanol. Therefore, Zr incorporated SBA-15 silica materials with two different amount of zirconia loadings were prepared by hydrothermal synthesis. In addition to them, sulfate modified forms (SO/Zr-SBA-15) were prepared by treating Zr-SBA-15 catalysts in 0.5 M and 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions respectively. These 6 catalysts were tested in the glycosidation of butanol and as product butyl glucosides were produced. The reaction tests were carried out in a 100 ml glass reactor at 117°C.

Catalysts properties were determined by different characterization techniques. The analysis showed that mesoporous, acidic catalysts were obtained and zirconium was incorporated into SBA-15 structure. While the surface area and pore diameter decreased by higher zirconium loading and sulfonation, acidity of the catalysts increased. The highest acidity was observed in 1.0 SO/Zr-SBA-15-(1.0) catalyst.

The formation of butyl glucosides was determined by HPLC analysis. Results showed that activity of the catalysts were different for the glycosidation reaction of butanol. The highest butyl glucoside yield was obtained with 1.0 SO/Zr-SBA-15-(1.0) catalyst, while the lowest yield was obtained with Zr-SBA-15-(1.0) catalyst. This was attributed to the higher acidity (2.35 mmol NH<sub>3</sub>/g cat.) and B/L ratio (1.97) of 1.0 SO/Zr-SBA-15-(1.0) catalyst with respect to the others. The reusability tests were performed up to 2 times for the catalyst with the best results. There was no major decrease (7%) in the product yields and this confirmed the stability and reusability of the catalysts.

**Keywords:** Glycosidation, Butyl glucoside, Zr-SBA-15, SO<sub>4</sub>/Zr-SBA-15

## ÖZET

### Zr-SBA-15 & SO<sub>4</sub>/Zr-SBA-15 KATALİZÖRLERİ İLE BÜTİL GLİKOZİT ÜRETİMİ

Bu çalışmanın amacı, bütül glikozit sentezi reaksiyonu için mezogözenekli katı asit katalizörler geliştirmektir. Bunun için; Zr-SBA-15 silika katalizörleri iki farklı miktarda zirkonyanın yapıya dahil edilmesiyle, hidrotermal sentez ile hazırlanmıştır. Bunlara ek olarak, Zr-SBA-15 katalizörlerinin sırasıyla 0.5 M ve 1.0 M H<sub>2</sub>SO<sub>4</sub> çözeltilerinde kimyasal işleme tutulmasıyla sülfat modifiye formları (SO/Zr-SBA-15) üretilmiştir. Bu 6 katalizör, bütül glikozit sentezi reaksiyonunda test edilmiş ve ürün olarak bütül glikozitler elde edilmiştir. Reaksiyon testleri, 117 °C'de 100 ml'lik bir cam reaktörde gerçekleştirilmiştir.

Katalizörlerin özellikleri, farklı karakterizasyon teknikleri ile belirlenmiştir. Analiz sonuçları, mezogözenekli, asidik katalizörlerin elde edildiğini ve Zr'nin SBA-15 yapısına başarıyla eklendiğini göstermiştir. Daha fazla zirkonyum yüklemesi ve sülfatlama ile yüzey alanı ve gözenek çapı azalırken, katalizörlerin asitliği artmıştır. En yüksek asitlik değeri 1.0 SO/Zr-SBA-15-(1.0) katalizöründe gözlemlenmiştir.

Bütül glikozitlerin oluşumu HPLC analizi ile belirlenmiştir. Bütül glikozit sentezi reaksiyonunda test edilen katalizörler farklı aktiviteler göstermiştir. En yüksek bütül glikozit verimi 1.0 SO/Zr-SBA-15-(1.0) katalizörü ile elde edilirken, en düşük verim Zr-SBA-15-(1.0) katalizörü ile elde edilmiştir. Bu durum diğer katalizörlere nispeten 1.0 SO/Zr-SBA-15-(1.0) katalizörünün daha yüksek asitlik değerine (2.35 mmol NH<sub>3</sub>/g cat.) ve B/L oranına (1.97) sahip olmasına bağlanmıştır. Yeniden kullanılabilirlik testleri, en iyi sonuçların elde edildiği katalizör ile 2 defaya kadar gerçekleştirilmiştir. Ürün veriminde önemli bir azalış (%7) gözlemlenmemiştir ve bu sonuç katalizörlerin dayanıklılığını ve tekrar kullanılabilirliğini doğrulamıştır.

**Anahtar Kelimeler:** Glikozidasyon, Bütül glikozit, Zr-SBA-15, SO<sub>4</sub>/Zr-SBA-15

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# CHAPTER 1

## INTRODUCTION

Alkyl glucosides are a class of non-ionic surfactants. They are widely used in cosmetics and detergents as surface active agent, emulgator for food and dispersant for pharmaceuticals. Alkyl glucosides are excellent surfactant, biodegradable, less toxic and sustainable. Therefore, they are preferably used chemicals in industries (Hill et al., 1997).

There is a growing interest in producing chemicals from biomass due to depletion of petroleum resources, environmental pollution problems and search for sustainable chemical processing. Carbohydrates is the most abundant biomass in nature to be used as raw material for several valuable chemicals production. Glucose as a subcategory of carbohydrates, is the most common monosaccharide in nature. For this reason; in order to diversify the uses of glucose, recent studies have focused on functionalization of glucose (Corma et al., 2007).

Acetalization of glucose by aliphatic alcohols produces alkyl glucoside. They consist of a hydrophobic alkyl residue derived from a fatty alcohol and a hydrophilic saccharide structure derived from glucose, that are linked through a glucosidic bond. Especially alkyl glucosides containing long carbon chains between 8 to 18 carbon atoms are most valuable due to their good surfactant properties, biodegradability and low toxicities (Villandier et al., 2010).

Glucose solubility is low in long chain alcohols. So, higher glucosides are produced in two steps. Firstly, butyl alcohol is used for acetalization of glucose in order to solve the solubility problem. Then; by transacetalization reaction with long chain aliphatic alcohols, alkyl glucosides containing long carbon chains can be produced (Li et al., 2012).

In industrial applications, sulfuric acid, which is homogeneous catalyst, is used in order to produce alkyl glucoside. But usage of homogeneous catalyst has so many drawbacks such as waste treatment, separation from products and purification. On the other hand, heterogeneous catalyst usage in this reaction has several advantages such as easy separation, reusability, no solvent requirement and tunable textural properties (Hill et al., 2007).

In the literature, reaction parameters such as reactant ratio, catalyst type, reaction temperature and reaction time were investigated. The effects of the catalyst selection for the reaction, and the effects of the catalyst preparation techniques on the acidity and surface properties of the catalysts were also researched in the literature. According to results that obtained from these researches, there is no such heterogeneous catalyst that is good enough to perform this reaction with high selectivity and conversion.

In this study, mesoporous solid acid catalysts were prepared for glycosidation reaction of butanol. In order to perform this, zirconium incorporated SBA-15 catalyst was prepared by hydrothermal synthesis. Sulfated forms of Zr-SBA-15 prepared by different  $\text{H}_2\text{SO}_4$  concentrations, were also synthesized and used as catalyst in glycosidation reaction. The effect of the catalyst type on conversion and selectivity was investigated. Consequently, the effects of surface area, pore volume, pore diameter, acidity and elemental composition were discussed.

## CHAPTER 2

### BACKGROUND

#### 2.1. Alkyl Glucosides

Due to the depletion of petroleum resources, environmental pollution problems and search for sustainable chemical processing, there is an increasing interest in producing chemicals from biomass. Carbohydrates are one of the most common biomass in nature. They can be used as raw material for many valuable chemicals production. Glucose is a type of carbohydrate which can be modified to alkyl glucoside by glycosidation reaction. The fact of alkyl glucoside can be obtained from renewables raw materials, makes them commercially and ecologically a center of interest (Corma et al., 2007).

Alkyl glucoside belongs to non-ionic biodegradable surfactant group. They are produced by the reaction of glucose and fatty alcohol in the presence of acid catalysts at elevated temperatures. Since alkyl glucosides are comprised of hydrophilic glucose and hydrophobic alcohol, they contain both hydrophilic and hydrophobic moieties.

As a surfactant, alkyl glucosides lower the surface tension between two phases. Besides they are excellent surfactant, they are biodegradable, less toxic and sustainable. They produce rich and stable foam; thus show strong deterative power. Also, they are safe for sensitive skin and eye (Li et al., 2012).

In chemical industry market, production of surfactants has a significant share with an annual production of about 14 million tons in 2011. Production of surfactants from biomass attracts wide range of attention due to the increasing prices of oil barrel and consumers demand for the supply of greener chemicals. As an example, between 2008 and 2013, the annual growth rate of bio based surfactants in Europe was 3% (Boissou et al., 2015).

Companies such as Rohm & Haas, BASF, SEPPIC, Procter & Gamble, Henkel started programs to produce alkyl glucosides for cosmetic and detergent industries in the 1970s. Alkyl glucosides enhance the formation of foams and preferred on account of safe for sensitive skin. Alkyl glucosides are used in many products such as cosmetics, detergent, cleaning agents, medicines additives and industrial emulsifier. The applications

of alkyl glucosides are wide and as the technology develops, more areas will be interested in alkyl glucosides. Due to their physicochemical properties, alkyl glucosides show interesting effects for various applications (Corma et al., 2007; Li et al., 2012).

## 2.2. Fischer Glycosidation

Earlier glycosidation reactions were performed by various techniques. Then, Emil Fischer proposed a fundamentally different approach to the synthesis of alkyl glucosides in 1893. Afterwards, acid catalyzed reaction of glucose and alcohol is known as Fischer glycosidation. Fischer glycosidation refers to the formation of a glucoside by the reaction of an aldose or ketose with an alcohol in the presence of an acid catalyst.

Koenigs-Knorr method is the other main procedure that can be applied to produce alkyl glucosides. But comparing to Fischer glycosidation, Koenigs-Knorr is more complex and costly method. Also, the other advantage of Fischer synthesis is that the properties such as hydrophilicity and water solubility can be controlled precisely. Also, several homogeneous or heterogeneous acids such as silica-alumina, ion exchange resins, zeolites, mesoporous materials, mineral and organic acids can be used as catalyst (Villandier et al., 2010; Hill, 1997).

In Fischer synthesis, the reactants of the alkyl glucoside synthesis are carbohydrate and fatty alcohol. Since both polymeric and monomeric carbohydrates are suitable as raw materials for the production of alkyl poly glucosides, sugars such as fructose, mannose, xylose and disaccharides like lactose, cellobiose, and maltose can be used as reactant for the production of alkyl glucosides. Usually, glucose is the preferred carbohydrate for glycosidation reaction. As the carbohydrate source; corn, wheat and potatoes which are rich in starch can be used for this process. Cellulose which is a polymer of glucose monomers may also be used as carbohydrate source. Fatty alcohol can be obtained by synthetically from petrochemical sources or they can be derived from the fermentation of sugars beet, sugarcane, corn, wheat, lignocellulosic biomass, starch-based waste packing peanuts and agricultural wastes (Corma et al., 2007; Değirmenci, 2010; Hill, 1997).

There are two products in glycosidation reaction and they are isomers. Alkyl glucofuranoside appears as a primary product, while alkyl glucopyranoside is secondary and stable product. Reaction mechanism suggests that, formation of alkyl glucofuranoside which is five membered ring compound followed by isomerization to the alkyl

glucopyranoside product, six membered ring compound. Synthesis mechanism of the isomers of butyl glucoside is shown in Figure 2.1. Basically, process follows this order. In Fischer glycosidation reaction, the first step is protonation of sugar by an acid catalyst and this leads to the formation of an oxonium cation after the loss of water. Then, acetalization of glucose occurs by a nucleophilic attack of alcohol (Villandier et al. 2011).

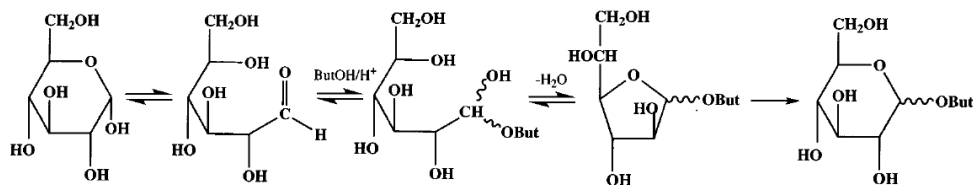


Figure 2.1. Synthesis mechanism of butyl glucofuranoside and butyl glucopyranoside

(Source: Corma et al., 1996)

Alkyl glycosidation reaction by Fischer synthesis can be applied either direct synthesis or two stage transacetalization process. Solubility of glucose in long chain alcohol is low, so it leads mass transfer limitation problems for glycosidation reaction. But the two stage transacetalization process needs more equipment than the direct synthesis. In two step process, firstly the carbohydrate reacts with a short chain alcohol such as methanol and butanol. These lower glucosides are quite better soluble in alcohol and can be used as intermediates for the production of higher alkyl glucosides. In the second stage, the short chain alkyl glucoside is transacetalized with a relatively long chain alcohol such as octyl and dodecyl alcohol as shown in Figure 2.2. On the other hand, in terms of equipment, direct synthesis is more straightforward, since the two stage transacetalization process needs more elaborate system. After the first step, catalyst deactivation necessitates separation and addition of new catalyst to the system (Hill et al., 1997).

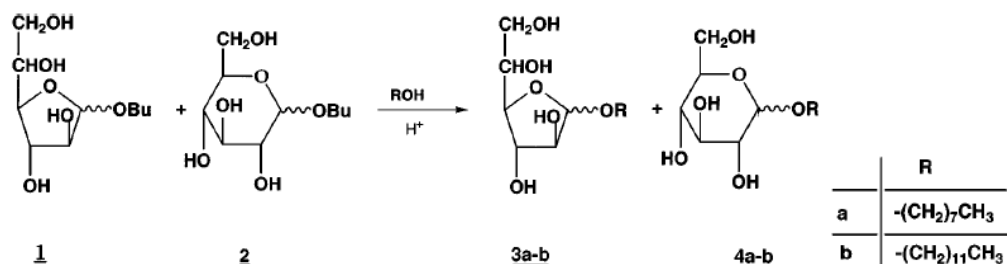


Figure 2.2. Transacetalation

(Source: Corma et al., 1998)

### 2.2.1. Catalyst Types

Glycosidation reaction of fatty alcohol needs acidic medium, thus acidic catalysts are required for conventional alkyl glucoside production processes. There are three ways to catalyze reactions which are homogeneous, heterogeneous and enzyme catalysts. The usage of enzyme catalysts in alkyl glucoside synthesis are limited to the laboratory. Due to the problems of availability of suitable enzyme and the high manufacturing costs, enzyme catalysts are not preferred in industrial level (Hill et al., 1997).

Most of the liquid phase industrial reactions use homogeneous catalysts such as inorganic and mineral acids. These catalysts need neutralization steps and separation units in order to isolate product. The all production processes result in enormous amount of hazardous waste and disposal of these wastes cost more than the value of the product. The other drawback of homogeneous catalysts is their corrosiveness. Because of these reasons, emission regulations have been developed in recent years and it leads industries to search for innovative clean technologies as heterogeneous catalyzed process. In most of the reactions, usage of solid heterogeneous catalyst is advantageous over homogeneous catalyst since it prevents the formation of oligomers. Due to shape selectivity of the heterogeneous catalyst, the other bulkier transition states productions become limited. So, the undesired product formations can be restrained. However, heterogeneous catalysts mostly suffer from low productivity and deactivation. These obstacles prevent the usage of solid heterogeneous catalysts in industrial level (Wilson et al., 2000; Corma, 2007; Karam, 2017).

The one of the important parameter of the reaction is the selection of the catalyst. Depend on the reactants, medium of the reaction, hydrophilic-hydrophobic characteristics of the materials; appropriate catalyst should be selected. In glycosidation reaction, acidity of the catalyst is important, since the reaction occur in an acidic medium. The amount, type and strength of the acidic site is extremely effective on the activity of the catalyst. There are two types of acidity which are Bronsted and Lewis acidic sites on the heterogeneous catalysts surface. Bronsted acidity arises often from Lewis acidic sites as shown in Figure 2.3. These acidic sites are essential for the activity and selectivity of the glycosidation reaction. Development of selective catalysts for the glycosidation process needs optimization of the catalyst in terms of amount of acidity, type of the acidic sites and strength. For example, optimization is not well enough, it can lead polymerization or etherification reactions. (Wilson et al., 2000; Do, 2012).

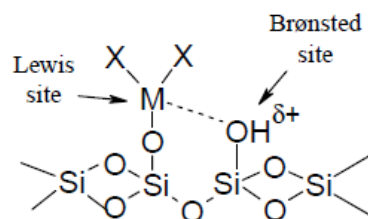


Figure 2.3. Brønsted acidity arising from inductive effect of Lewis acid center coordinated to a silica support.

(Source: Wilson et al., 2000)

### 2.2.2. Reaction Parameters

The type and concentration of the products obtained from glycosidation reaction depend on process parameters such as temperature, pressure, reaction time, molar ratio of reactants and catalyst. By changing these parameters, undesired products can be eliminated and ratio of the products become adjustable according to the needs of the final product (Hill et al., 1997).

The production of alkyl glucosides based on short chain alcohols lead less by products comparing to long chain alcohols. Also, this causes decrease of molar yield of the main product. Because of that, transacetalization reaction much more preferred than direct glycosidation reaction in industry. Between the carbohydrates and alcohol, hydrophilic-lipophilic interactions affect the activity of the reaction. By using alcohol with longer chain, lipophilic properties of the alcohol increase and interaction between carbohydrates and alcohol becomes difficult. So, activity of the reaction is affected negatively. (Villandier et al., 2010; Hill, 1997)

In glycosidation reaction, typical reaction pressure in both direct synthesis and transacetalization are between 2 and 10 kPa. As the Figure 2.4. shows, higher yield is obtained as the pressure decreases. Best reaction pressure for producing alkyl glucoside should be around 3-4 kPa (Wang et al., 2015).

Temperature has significant effect on the activity and selectivity of the glycosidation reaction. When the temperature is below 100°C secondary products are low. At the same time, reaction time becomes longer and the rate of the reaction decreases significantly. At high temperatures large amount of water can be produced. Necessary precautions should be taken in order to remove the excess water from the system. Side reactions could be formed in the presence of water in the system. This can result in with



the formation of polymers such as polydextrose. Design of the reactor, heat exchange area, evaporation area and stirrer affect the evaporation of water efficiency.

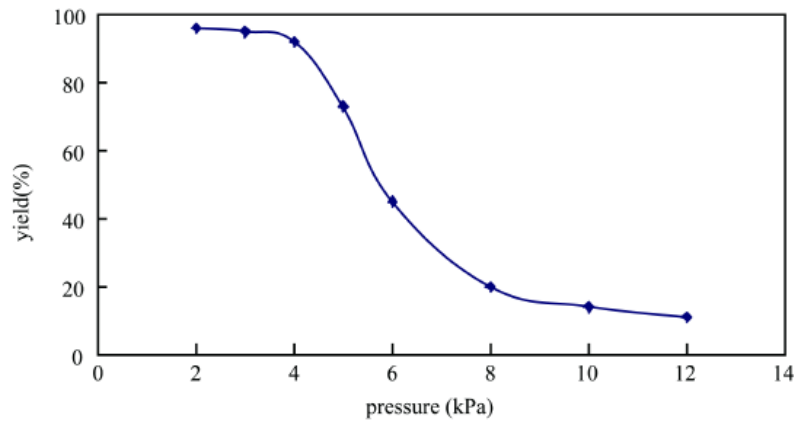


Figure 2.4. The influence of pressure on the yield of alkyl glucosides.

(Source: Wang et al., 2015)

## CHAPTER 3

### LITERATURE SURVEY

There are numerous studies about glycosidation reaction of alcohols in the literature. In this section, most related studies are selected and summarized.

#### 3.1. Fischer Glycosidation Reaction

Corma et al. (1996) studied the Fischer glycosidation of butanol, using different acid zeolites as catalysts. 5 different zeolites (HY, ZSM-5, H-mordenite, MCM-22, H-Beta) were synthesized for testing in the reaction. The reaction was carried out at 110°C for 4 h and as products butyl glucofuranoside and butyl glucopyranoside were obtained.

The effect of catalyst acidity on the activity was investigated and results showed that catalyst activity increased with increasing amount of acid, but especially the Bronsted acid sites. Also, it was found out that Bronsted acidity of the catalyst was not the only accountable factor for the catalytic activity. Topology of the catalysts such as large cavities and pore windows positively affected the diffusion of the products and increased the catalytic activity. For example; HY, which is 12-member ring unidirectional zeolite with cavities, showed better activity than MCM-22; although it had less Bronsted acidity (Table 3.1.). In order to compare homogeneous and heterogeneous catalyst, the reaction was carried out using p-toluenesulfonic acid and the initial disappearance rate of glucose was 30.36 mol h<sup>-1</sup> which was higher than HY zeolite. On the other hand, when amorphous silica-alumina was used, reaction rate decreased to 0.05 mol h<sup>-1</sup>g<sup>-1</sup>.

Table 3.1. Initial rate ( $r_{O1}$ ) of butyl furanoside per Bronsted acid site in the presence of different zeolites

(Source: Corma et al., 1996)

Zeolite	Brønsted acidity <sup>a</sup> (Ba)	( $r_{O1}$ )/(Ba) (mol h <sup>-1</sup> /μmol Py) × 10 <sup>2</sup>
MCM-22	41.28	2.03
HY-100	21.14	4.49
H-ZSM-5	21.14	2.31
H-Beta	27.18	2.43
H-Mordenite	21.14	0.85

<sup>a</sup>Acidity (μmol Py/g catalyst) of the zeolite catalysts

Also, the effect of adsorption properties of catalysts was investigated by comparing HY zeolites with different Si/Al ratios (4 to 27). Results showed that catalyst stability was increased by the zeolites with higher Si/Al ratio. Because of their more hydrophobic characteristic, they were less affected by the diffusional limitations which was caused by the strong adsorption of the hydrophilic glucose molecules. This hypothesis was consistent with the fact that H-Beta zeolite which had higher Si/Al ratio and therefore more hydrophobic character, achieved higher final conversion than HY zeolite, even though the number of acid sites was much lower.

Influence of the butanol/glucose ratio on the initial rates of butyl glucofuranoside and butyl glucopyranoside was studied. The result implied that with butanol/glucose ratios of 20 and 40, 100 % conversion and selectivity can be possible in the presence of H-Beta zeolite. Butanol glucose ratio of 40 was chosen to avoid glucose solubilization problem and the formation of oligosaccharides. 3% butyl glucofuranoside and 95% butyl glucopyranoside yield was obtained with H-Beta zeolite. In total, 98% butyl glucoside yield was achieved. This indicated that formation of oligosaccharides was seriously restricted inside the pores of H-Beta zeolite, so higher butyl glucoside selectivity obtained.

Cambor et al. (1997) investigated the role of crystal size and hydrophobicity of zeolite H-Beta as a catalyst for the preparation of butyl glucoside surfactant by two series of zeolites (PS: obtained by dealumination, and S: free of silanol groups) with different Si/Al ratio (12 to 260) and crystal sizes (0.05–0.90  $\mu\text{m}$ ). The reaction was carried out at 120°C for 4 h and two isomers of butyl glucoside were produced.

The effect of temperature and catalyst amount on the reaction rate and selectivity were investigated. Results showed that total yield was not affected by temperature and catalyst amount rise, but butyl glucopyranoside was favored as it is shown in Table 3.2.

Table 3.2. Influence of temperature and percentage of H-Beta zeolite catalyst on the rate of the glycosidation reaction

(Source: Cambor et al., 1997)

Temperature (K)	Catalyst (%) <sup>a</sup>	$r_0 \times 10^2$ (mol min <sup>-1</sup> )	Yield <sup>b</sup>	
			<b>2</b>	<b>3</b>
383	1.5	1.15	34	65
393	1.5	5.06	20	78
393	3.0	10.31	6	90

<sup>a</sup>Percentage of catalyst related to the total weight of the reactants.

<sup>b</sup>At 4-h reaction time, (**2**) butyl glucofuranoside, (**3**) butyl glucopyranoside

As shown in Table 3.3., 0.35  $\mu\text{m}$  and below crystallite size led to higher initial reaction rate. The results implied that, due to the diffusional restrictions, six membered ring butyl glucopyranoside was much more affected than five membered ring butyl glucofuranoside by crystallite size increment.

Table 3.3. Influence of the zeolite crystal size on the initial reaction rates ( $r_0$ , mol min<sup>-1</sup> g<sup>-1</sup>) and on the products distribution at 60% glucose conversion

(Source: Cambor et al., 1997)

Catalyst	Crystal size ( $\mu\text{m}$ )	$r_0 \times 10^4$ (mol min <sup>-1</sup> g <sup>-1</sup> )	Yield (%)		
			2	3	2/3
H beta-1	0.05	4.9	50	10	5.0
H beta-2	0.35	5.2	48	12	4.0
H beta-3	0.60	3.7	55	5	11.0
H beta-4	0.90	1.8	57	3	19.0

(2) butyl glucofuranoside, (3) butyl glucopyranoside

Glycosidation reaction needs acidic catalysts in order to take place, so it was expected that the catalyst with the lowest Si/Al ratio gives the highest reaction rate, since the acidity was higher with respect to the others. However, instead of Beta (PS)-5 catalyst, Beta (PS)-7 catalyst with less acidity showed the highest reaction rate (Table 3.4). The reason for this unexpected fact was attributed to the effect of hydrophilicity of the catalyst. Then, acidity was not considered the only parameter in reaction rate. Strong adsorption of glucose blocked the pores and active sites, so diffusion and adsorption of butanol became limited. By dealumination; Si/Al ratio increased, thus hydrophilicity of catalyst decreased, and it helped the desorption of glucose from the catalyst pores.

Table 3.4. Influence of the framework Si/Al ratio and Bronsted acidity of the Beta zeolite on the initial rate and yields in the glycosidation reaction

(source: Cambor et al., 1997)

Catalysts	Si/Al	B.A. <sup>a</sup>	$r_0 \times 10^4$ (mol min <sup>-1</sup> g <sup>-1</sup> )	Yield (%)	
				Butyl glucofuranoside	Butyl glucopyranoside
Beta (PS)-5	52	78.52	2.14	54	42
Beta (PS)-6	88	66.44	3.48	63	35
Beta (PS)-7	118	55.56	3.68	55	42
Beta (PS)-8	123	53.15	2.43	66	32
Beta (PS)-9	140	48.32	2.13	65	25

<sup>a</sup>Bronsted acidity (mmol Py/g catalyst)

Corma et al. (1998) compared one-step direct reaction of a higher alcohol with glucose and two-step process glycosidation. As long-chain fatty alcohol, 1-octanol and 1-dodecanol were used and influences on the preparation of alkyl glucoside were examined.

In the presence of activated H-Beta zeolite, preparation of butyl glucoside and then the transacetalation process with octyl or dodecyl alcohol carried out at 120° C for 4 h. Likewise, same conditions were applied for one-step direct glycosidation. Octyl and dodecyl glucosides were produced as primary products with both methods. The proposed reaction mechanism is given in Figure 3.1. Formation of octyl glucofuranoside can occur by the transacetalization of butyl glucofuranoside. While, octyl glucofuranoside can be obtained in several different ways (B, D and E).

Experiments showed that the initial rate of disappearance of butyl glucosides was strongly influenced by the feed composition. As can be seen in Table 3.5, higher amount of butyl glucofuranoside gave rise to a higher reaction rate and total conversion over shorter reaction time.

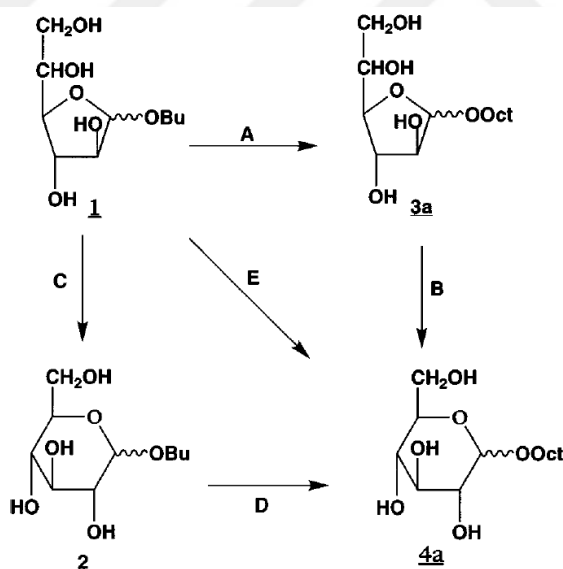


Figure 3.1. The transacetalization of the butyl glucosides

1: butyl glucofuranoside, 2: butyl glucofuranoside, 3a: octyl glucofuranoside, 4a: octyl glucofuranoside

(Source: Corma et al., 1998)

The temperature effect on the rate was investigated in transacetalization of butyl glucosides reaction. Results showed that the temperature increase from 110° to 120° C resulted in 2.5 increase in the rate of butyl glucoside disappearance. Higher reaction temperature increased the side reactions such as oligomerization, thus poor quality

product was obtained. The effect of the chain length of the alcohol was also studied. Dodecyl alcohol, which has longer chain, needed longer reaction time to reach the same level of conversion. Due to the less solubility of alkyl glucoside in the dodecyl alcohol.

Table 3.5. Initial disappearance rates of butyl glucosides, starting from two different initial mixture compositions in butyl glucosides

(Source: Corma et al., 1998)

Compounds	Initial mixture composition	Initial disappearance rates of butylglucosides ( $\text{mol h}^{-1} \text{g}^{-1}$ ) $\times 10^3$
<u>1</u>	70	15
<u>2</u>	30	
<u>3a</u>	0	
<u>4a</u>	0	
<u>1</u>	10	5.2
<u>2</u>	90	
<u>3a</u>	0	
<u>4a</u>	0	

1. butyl glucofuranoside 2. butyl glucopyranoside

Deactivation of the catalyst was tested with or without addition of fresh catalyst during the transacetalization step. The rate of the butyl glucoside disappearance was increased by 25 % with the addition of fresh catalyst. Finally, it was concluded that, because of the deactivation of the catalyst, difficulty in separation of products and requirement of new catalyst addition, two-step glycosidation is more disadvantageous than the one-step. In one-step direct glycosidation reaction of octyl and dodecyl alcohol, good conversion and excellent selectivity can be obtained, if incremental addition of glucose is applied in long enough time.

Chapat et al. (1999) studied the glycosidation reaction over various dealuminated HY zeolites with Si/Al ratios from 2.5 to 100 and they were received commercially. The reaction was carried out in a batch reactor by adding D-glucose and n-butanol, under mixing of 1000 rpm at 110°C using 6 wt.% of catalyst. The effect of kinetics, mechanism, stereo electronic, and micro reversibility were investigated. The reaction scheme was proposed for glycosidation reaction, from the systematic study of the glycosidation reaction (Figure 3.2.). It suggested that both successive and parallel reactions occurred at the same time in the system. Since butanol was used as alcohol, the primary products of the study were butyl glucofuranoside and butyl glucopyranoside.

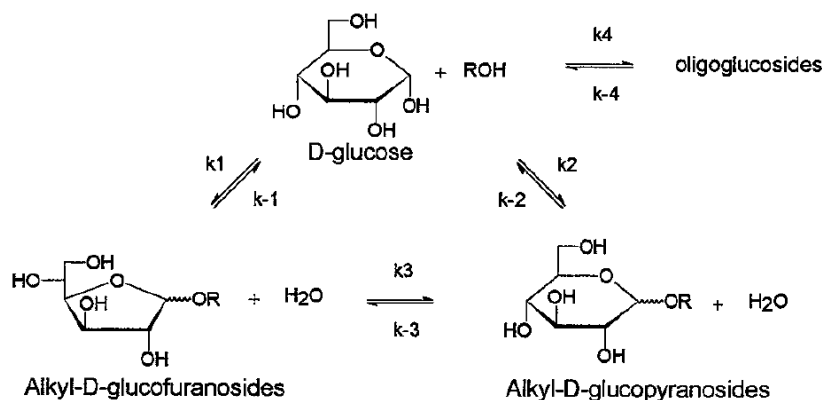


Figure 3.2. Simplified reaction scheme for glycosidation of glucose with butanol.

(source: Chapat et al., 1999)

According to the results, higher Si/Al ratios increased the hydrophobicity. Thus, the adsorption of glucose molecules decreased. On the contrary, lower Si/Al increased the hydrophilicity, so the adsorption of glucose molecules increased excessively and this caused diffusion and adsorption limitation of butanol. Also, butanol/glucose ratio was changed between 5 to 40, in order to study the effects of ratio on conversion and selectivity. The reaction rates at different initial concentrations in glucose were calculated and results indicated that the rate increased up to 0.4 M initial glucose concentration, then decreased. Temperature effect on the reaction rates were investigated (90°-110°C). Results showed that the rate was positively affected by the temperature increment.

The reaction carried out with HY zeolite gave high butyl glucoside yield (8% butyl glucofuranoside and 81% butyl glucopyranoside). HY zeolite was then compared with H-Beta zeolite and p-toluenesulfonic acid. Almost complete conversion of glucose was obtained for all of these catalyst types. In addition, results showed that stereoselectivity ( $\alpha/\beta$ ) of glucopyranoside was much higher for H-Beta zeolite and it was attributed to shape selectivity of the catalyst. In this study, shape selective microporous catalyst was used purposefully. Thus, comparing to homogeneous catalyzed reaction, the amount of oligomers significantly decreased.

Climent et al (1999) studied the Al-MCM-41 mesoporous materials as catalysts for the synthesis of butyl glucosides. The catalysts were prepared with different Si/Al ratios ranging from 15 to 50 by hydrothermal method and their properties are given in Table 3.6. The glycosidation reaction was performed in a magnetically stirred (600 rpm) 100 ml batch reactor at 120°C for 4 h. The only products observed over the Al-MCM41 catalyst were isomers of butyl glucoside. As the reaction progressed, butyl

glucofuranoside was converted to butyl glucopyranoside. They proposed the reaction mechanism (Figure 3.3.), involving the fast formation of the five membered ring compound, followed by the ring expansion to the pyranoside product.

Table 3.6. Synthesis conditions, chemical composition, pore diameter, and surface area of the catalysts

(Source: Climent et al., 1999)

Catalysts	<i>n</i>	<i>x</i> (10 <sup>3</sup> )	Crystallization			Pore	
			T (K)	Time (days)	Si/Al	diameter (nm)	S (m <sup>2</sup> /g)
MCM41-1	16	3.33	423	5	14	4.9	720
MCM41-2	16	2.0	423	5	26	5.4	624
MCM41-3	16	1.0	423	5	50	5.3	753
MCM41-4	16	1.0	408	1	51	4.5	835
MCM41-5	16	1.0	408	3	50	2.5	880

\*Synthesis gel formulation: SiO<sub>2</sub>,0.28; TMAOH, 0.12; C<sub>n</sub>TABr, 26.2; H<sub>2</sub>O, xAl<sub>2</sub>O<sub>3</sub>

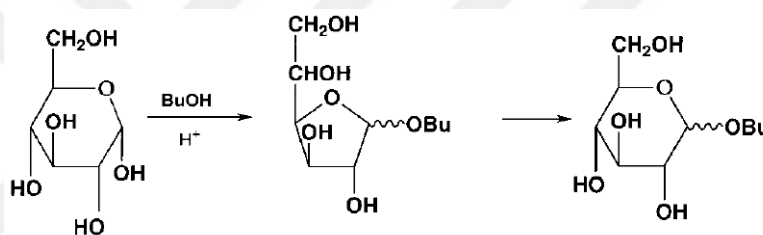


Figure 3.3. The reaction scheme for butyl glucoside formation

(Source: Climent et al., 1999)

For comparison H-Beta zeolite was used. According to the results, H-Beta zeolite was more active than the MCM-41 and it was attributed to the bridging hydroxyl groups, which were also related to the presence of tetrahedrally coordinated Al (Bronsted acid sites) in the walls of MCM-41. The influence of the chemical composition (Si/Al) and pore dimensions on activity and selectivity was investigated. The framework Si/Al ratio of molecular sieves was not only responsible for the acidity but also for the hydrophobicity. As can be seen in Table 3.7., all of the catalysts had Bronsted and Lewis acid sites, but activity was not affected as expected. Due to the different polarities of the two reactants and the product, adsorption-desorption properties of the material were important in this reaction. Glucose is hydrophilic and on the contrary n-butanol is hydrophobic compound.

The larger the diameter of the pore at the same level of Al content, the more active was the final catalyst. In the case of the MCM-41-3 sample with a Si/Al ratio of 50 and



5.3 nm pore diameter, some glucose was still strongly adsorbed in the pores of the catalyst. These strongly adsorbed molecules decreased the mean effective path way in the pores, therefore caused diffusional limitations. The larger pore diameters were also positively affected the ratio of pyranoside to furanoside. Lastly, reusability of the catalysts was tested and according to the results, activity slightly decreased due to the loss of crystallinity and surface area.

Table 3.7. Acidity of the catalysts, rate of glucose disappearance, yield and conversion in the glycosidation reaction

(Source: Climent et al., 1999)

Catalyst	423 K		$r_o \cdot 10^4$ (mol min <sup>-1</sup> g <sup>-1</sup> )	Yield (%)		Conversion (%)
	B.A. <sup>a</sup>	L.A. <sup>a</sup>		<u>3</u>	<u>4</u>	
MCM41-1	11.8	37.8	2.7	55	42	97
MCM41-2	8.3	11.0	3.13	61	33	94
MCM41-3	7.2	8.9	3.68	39	59	98
MCM41-4	7.1	10.6	2.30	58	36	94
MCM41-5	6.0	10.6	1.38	55	25	80

<sup>a</sup>Bronsted acidity and Lewis acidity (mol Py/g catalyst)

3. butyl glucofuranoside, 4. butyl glucopyranoside

Andrade et al. (2000) investigated the Al-MCM-41 as catalyst for one step direct glycosidation of butyl and octyl alcohol. Al-MCM-41 catalyst, prepared with different Si/Al ratio (5-250), was characterized by the structure, acidity and catalytic activity for the production of butyl and octyl glucosides. The glycosidation reaction was carried out in 10 ml batch reactor at 110°C for 4 h. Before using in reaction, glucose was penta acetylated in order to prevent ring chain tautomerism and anomerization.

Results showed that Al-MCM-41 catalysts with different pore diameter (38-46 Å), and surface area (575-990 m<sup>2</sup>/g), were synthesized successfully. Butyl and octyl glucosides were obtained as major products of the glycosidation reaction.

According to the analysis, aluminum content increased the catalyst activity. By increasing Al contents in the catalyst, the amount of Bronsted and Lewis acid sites increased, on the contrary strength of these sites decreased. Acid strength of the active sites influenced the catalytic performance of the reaction. It was found out that Bronsted sites were weak and medium strength, contrarily stronger Lewis acid sites were present. Also the influence of the alcohol/glucose ratio was investigated between 15-40. Higher conversion was obtained by the alcohol/glucose ratio of 40 due to the avoidance of the

solubilization problem of glucose by increasing alcohol volume as solvent. As opposed to expectations, higher conversion was obtained by octanol (78%) rather than butanol (28%). But, selectivity of pyranoside (95%) was higher for glycosidation reaction of butanol. It was attributed to pore size and morphology of the molecular sieve catalysts.

Kim et al. (2009) studied the enzymatic synthesis of alkyl glucosides using *Leuconostoc mesenteroides* dextransucrase with sucrose and various alcohols. The main objective of this study was to achieve the synthesis of methyl glucoside and ethyl glucoside from sucrose in a biphasic medium.

Methanol, ethanol, 1-propanol, 1-butanol and 3-methyl-1-propanol were tested as alcohol sources. The results showed that alkyl glucosides were obtained with a yield of 30% with primary alcohols, but secondary alcohols or tertiary alcohols gave yields below 5%. The highest yield obtained was 50% using 1-butanol. These results showed that dextransucrase is a more suitable enzyme than frequently used enzymes (*Aspergillus niger*,  $\beta$ -transglucosidase) for such reactions.

Villandier et al. (2011) studied the synthesis of long chain alkyl glucoside from cellulose by two different methods in the presence of ionic liquid and Amberlyst-15 catalyst. First method was the direct transformation of cellulose to alkyl glucosides. The other method was the two step reaction: firstly, transformation of cellulose to methyl glucoside then transacetalation with longer chain alcohols as illustrated in Figure 3.4.

Results showed that during the direct transformation of cellulose into alkyl glucosides, the hydrolysis of cellulose continued as Fischer glycosidation. In one-step glycosidation of cellulose with octanol, 98% cellulose conversion and 70% alkyl glucoside yield by mass were obtained.

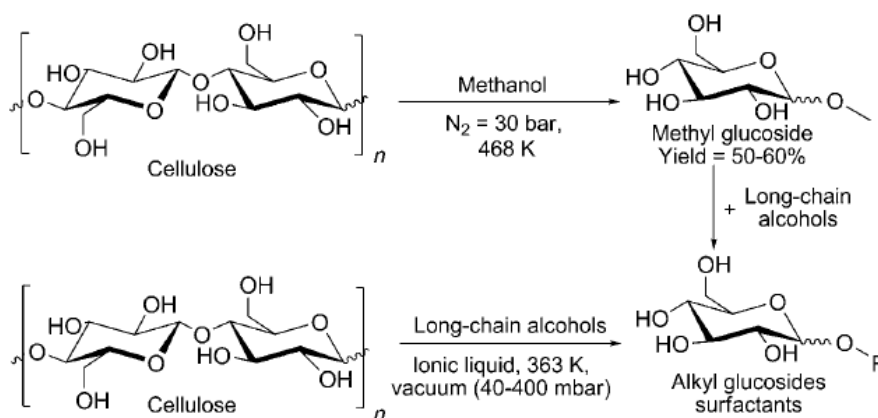


Figure 3.4. The transformation of cellulose into alkyl glucosides by following two routes.

(Source: Villandier et al., 2011)

Butanol, hexanol, octanol, decanol and dodecanol were used for comparison. According to the study, solubility of alkyl glucoside and critical micelle concentration were negatively affected by the length of alkyl chain. Also, the yield of alkyl glucoside decreased as the chain length of alcohol became longer. This was attributed to the hydrophilic-lipophilic interactions between the carbohydrates and alcohol. Using longer chain alcohol increased the lipophilicity and this led to weak contact between the carbohydrates and alcohol. Therefore, low yield was obtained.

Heteropoly acid ( $H_3PW_{12}O_{40}$ ) and H-Beta zeolite were also tested for comparison of the different catalyst types. In the presence of Amberlyst-15, 82% global yield was obtained for the direct transformation of cellulose to butyl glucoside reaction. On the other hand, the global yield decreased to 38.9 % when H-Beta zeolite was used as catalyst.

Also results showed that; in the transacetalation process, the amount of methyl glucofuranoside positively affected the amount of the furanoside isomer in the final product.

Li et al. (2012) synthesized dodecyl glucoside by glucose and dodecanol using p-toluenesulfonic acid as catalyst. The reaction carried out at 120°C and 5 kPa for 4 h. The effects of catalyst type, reactant ratio, reaction temperature and pressure were investigated.

As catalyst dodecyl benzene sulfonic acid, p-toluenesulfonic acid and sulfuric acid were used for comparison purpose. In terms of reaction rate, product color and the yield of dodecyl glucoside, p-toluenesulfonic acid gave the best results. Effect of mol ratio of dodecanol and glucose was studied. Dodecyl glucoside yield increased up to 6:1 ratio then decreased. It was attributed to lower concentration of catalyst due to the excessive alcohol.

The effect of catalyst/glucose mass ratio was also investigated. The yield of dodecyl glucoside increased up to 0.008:1 mass ratio, then decreased. This was explained by the fact that large doses of catalyst lead to react rapidly, therefore much water cannot eliminate promptly in a short time. In the water environment, sticky polysaccharide even agglomerate carbonization could be formed. So the dodecyl glucoside yield and the quality of the products were seriously influenced.

The reaction temperature was studied between 105°-125° C and the results showed that dodecyl glucoside yield reached maximum at 120°C, then the yield decreased as the temperature increased. Since the high temperature favored the side reactions, the yield of dodecyl glucoside was decreased at the temperatures higher than 120° C. The

effect of reaction pressure was researched with different reaction pressure. The reaction pressure affected the water concentration by causing dehydration, therefore dodecyl glucoside yield was influenced. It was found out that the most suitable reaction pressure was 5 kPa.

Chung et al. (2016) studied the various microporous catalysts with different acidity and pore topology in order to perform one step glycosidation of octyl alcohol with high selectivity and conversion. Y and Beta zeolite were purchased, while ZSM-5 synthesized by hydrothermal synthesis. Different Si/Al ratio (3-25), oxygen ring (8, 10 and 12), pore size (2.5-7 Å), pore volume (0.12-0.24 cm<sup>3</sup>/g) and surface area (413-577 m<sup>2</sup>/g) were obtained. The reaction performed with glucose and octanol at 130°C for 5 h at 600 rpm stirring rate.

Main products of this reaction were isomers of octyl glucofuranoside and octyl glucopyranoside which was primary and unstable product and the other was secondary and stable respectively. Yields of octyl glucoside which was summation of octyl glucofuranoside and octyl glucopyranoside, on the zeolite catalysts were high above 75%. And the highest yield of octyl glucoside (85%) was obtained on HY zeolite. Results also showed that conversion of glucose increased with proceeding of reaction and after 4 h, it reached to equilibrium.

Conversion of glucose with loading amount of catalyst was investigated by ZSM-5 zeolite. The conversion was over 85% when 1.0 g catalyst was loaded. According to the study, when the Si/Al ratio increased, the amount of acidity decreased and consequently conversion of glucose decreased. Lewis and Bronsted acid sites were observed by IR spectra for all of the catalysts. Hydrophobicity was important for the adsorption properties of the reactants and products. Thus, the activity of the reaction can be increased. Temperature effect on conversion and yield was investigated. Increase in temperature (110-130°C) positively affected the activity of the reaction.

Strong acidity decreased the activity of the catalyst. On the other hand, increase of the amount of mild acid site, increased the conversion of the glucose. Selectivity of the isomers of the octyl glucosides were influenced by the pore volume, surface area, directional channel of pore, pore size and acidity. Wide pore volume increased the ratio of 6 membered pyranoside isomer compared to furanoside. Reusability of the catalysts was also investigated. The catalysts were washed, dried and calcined after the reaction and almost the same catalytic activity was obtained by the reuse of the catalysts.

### 3.2. Mesoporous Solid Acid Catalysts Tested in Other Reactions

As given before, different types of solid acid catalysts were tested in the synthesis of butyl glucosides. But, there is a progressing search on developing active, selective and reusable heterogeneous catalyst for the glycosidation reaction. The results of the previous studies showed that the catalysts used for alkyl glucoside synthesis should have high surface area and large pore size. Also, hydrophobic structure and Bronsted acid sites are essential for developing a promising catalyst.

By the discovery of MCM-41, mesoporous molecular sieves have attracted attention due to their catalytic activity in reactions and ability to separate bulky molecules from the system. Hydrothermal stability of MCM-41 catalyst is problematic, when it is used in a system involves steam or hot water. Researches continued to search for a new mesoporous catalyst, after the disadvantage of MCM-41 catalyst usage in aqueous reaction systems. After then, synthesis of a new mesoporous silica which is called SBA-15 was reported by Zhao et al. This material was synthesized by an organic copolymer which organize the structure of a polymeric silica precursor template. Stability of SBA-15 is much higher than MCM-41, since it has more regular structure and thicker walls. In fact, solely SBA-15 has poor catalytic activity. So, in order to obtain acid catalytic material, silica mesoporous molecular sieves can be doped with zirconium, vanadium, manganese and so on (Chen et al., 2001; Zhao, 1998; Fuxiang, 2007).

SBA-15 silica material was chosen for this study as catalyst support because of its hexagonal structure and narrow pore size distribution between 5 and 15 nm. In addition to that, zirconia can be integrated in the structure of SBA-15. Thus, acidity and stability of the catalysts improve by the zirconia loading on the catalysts. Several methods can be used to prepare silica-zirconia materials such as mechanical mixing of the component oxides, impregnation, co-precipitation method, depositing silica on the zirconia and sol-gel method. In this section, some of the studies related to the mesoporous solid acid catalyst testing in different reactions were summarized.

Zhao et al. (1998) investigated the synthesis of SBA-15 mesoporous silica that has 50 to 300 Å pores. Amphiphilic block copolymer was used to synthesize ordered hexagonal mesoporous silica structure with tunable uniform sizes up to 300 Å. SBA-15 catalyst showed great hydrothermal stability unlike the other mesoporous catalysts. During the synthesis process, temperature of the mixture was changed in order to find out the temperature effect. While under 25°C amorphous silica was obtained, above the 80°C

silica gel was formed. SEM and TEM images showed that many rope like domains aggregated into wheat like macrostructures. According to the analysis; mean pore size was 89 Å, pore volume was 1.17 cm<sup>3</sup>/g, BET surface area was 850 m<sup>2</sup>/g and pore wall thickness was 31Å. Unlike the other surfactants, block copolymers can be tunable by changing the composition molecular weight or architecture during the synthesis.

Chen et al. (2001) studied the synthesis of sulfated zirconia supported MCM-41, using one-step incipient wetness impregnation method. For comparison purpose, aluminum was used as promoter in sulfated MCM-41 catalyst. The catalysts were tested in isomerization of n-butane and the results showed that catalytic activity of the catalyst improved by the Al promotion on the catalyst. This state was explained by the fact that promotion of Al favors the metastable tetragonal phase of zirconia which is more catalytically active than the monoclinic phase.

MCM-41 supported sulfated zirconia had improved characteristics such as high surface area, high mesopore volume and good homogeneous dispersion of zirconia. On the other hand, MCM-41 catalyst with aluminum promoted sulfated zirconia gave better textural properties with high surface area (517 m<sup>2</sup>/g), large pore size (2.14 nm) and high pore volume (0.41 ml/g). According to the results, sulfur content was higher comparing the non-promoted sulfated zirconia modified MCM-41 catalyst. And it was concluded that in the structure and the surface aluminum stabilized the sulfur. SEM and TEM images showed that tubular morphology and well-ordered channels. According to TPD analysis, strong acid sites were present in the catalysts.

The effect of calcination temperature was investigated. Below 680°C, due to the less decomposition of zirconium sulfate and aluminum sulfate, low catalytic activity was observed in the reaction. On the other hand; above 740°C, less amount of surface retained sulfate ions, therefore activity of the catalyst was affected negatively. Deactivation was occurred due to the coke formation. Regeneration process of the catalyst was performed at 450°C for 3 h in flowing air and the activity of the catalyst was recovered successfully.

Chen et al. (2004) investigated the synthesis of Zr incorporated SBA-15 mesoporous materials in a self-generated acidic environment. Zr-SBA-15 silica materials with Zr content up to 0.1 Zr/Si atomic ratio and of well-ordered pore structure, high surface area, and narrow pore-size distribution were developed with no additional mineral acids.

For the synthesis of Zr-SBA-15, P-123, silica (TEOS), zirconium precursor (ZrOCl<sub>2</sub>.8H<sub>2</sub>O), and water were used in an atomic ratio of 0.017:1.0:(0-0.1):220

P123:Si:Zr:H<sub>2</sub>O. The mixture was stirred at 35 °C for 1 day and then hydrothermally reacted at 90 °C for another day in static conditions. The product was filtered, washed, dried and then calcined at 500 °C for 3 h. The results showed that the Zr contents analyzed by EDX were all greater than those by ICP-AES. It was concluded that the zirconium species were more concentrated near the surface of the mesostructured framework than inside the bulk.

High BET surface area (711-860 m<sup>2</sup>/g), large pore volume (0.78-1.0 cm<sup>3</sup>/g), narrow pore size distribution of ~ 2 nm and a narrow range of wall thickness (5.0-5.8 nm) were observed for all samples of Zr-SBA-15 materials. Addition to that no significant blockage of the pore or reduction in pore diameter was found on the Zr-SBA-15 samples.

Fuxiang et al. (2007) studied the high zirconium loading on SBA-15 catalyst, its characterization and catalytic performance after sulfonation. Incipient wetness method was used in order to sulfate SBA-15. The activity of the catalyst was tested on isomerization reaction of pentane.

N<sub>2</sub> adsorption-desorption showed that sulfated form of SBA-15 catalyst had very regular mesoporous channels and large pore size. Results indicated that increase of the Zr/Si ratio caused the decrease of surface area and mesopore volume of the catalyst. While the average thickness of the wall was 4 nm, pore diameter was 7 nm. The activity of the catalyst increased after sulfonation. On the contrary, the activity decreased by the surface area decrease. As conclusion, it was stated that sulfated Zr-SBA-15 catalyst was promising super acid catalyst.

Garg et al. (2009) investigated the acidity and catalytic activity of sulfated zirconia modified SBA-15 catalyst. Zirconia was dispersed in SBA-15 mesoporous material by urea hydrolysis method. It was found out that surface area, pore diameter and pore volume decreased by the sulfonation of Zr-SBA-15 catalyst. While Bronsted acid site increased by the sulfonation, Lewis acid site gradually decreased. Therefore, it can be deduced that some of the Lewis acid sites converted to Bronsted acid sites.

Activity of the catalyst was investigated using cumene cracking and esterification of cyclohexanol. Correlation of activity and acidity also studied. Results indicated that mainly Bronsted acidity controlled the reaction. In conclusion, surface area of zirconia inside SBA-15 catalyst and the ability to hold sulfate ion to create strongly acidic sites are the main factor to increase the activity of the catalyst.

Değirmenci et al. (2011) studied the sulfated zirconia modified SBA-15 catalyst for cellobiose hydrolysis. According to the results addition of zirconium decreased the

surface area of the catalyst. Lewis and Bronsted acid sites were observed in FTIR spectra. By sulfonation Lewis acid sites converted into the Bronsted acid sites. Sulfated form of zirconium modified SBA-15 showed better catalytic activity than non-sulfated form in hydrolysis of cellobiose reaction.

In many acid catalyzed reactions such as esterification and hydrocarbon isomerization, zirconia modified with sulfate anions show excellent performance as catalyst. From the Figure 3.5, it can be deduced that isolated  $Zr^{4+}$  species are suitable for the interaction between sulfate with zirconium species, then form strongly acidic sites. Sulfonation of isolated zirconium species in silica materials with high surface area can be a good method to synthesize a catalyst for acidic reactions (Kustov et al. 1994; Du, 2009; Değirmenci, 2010).

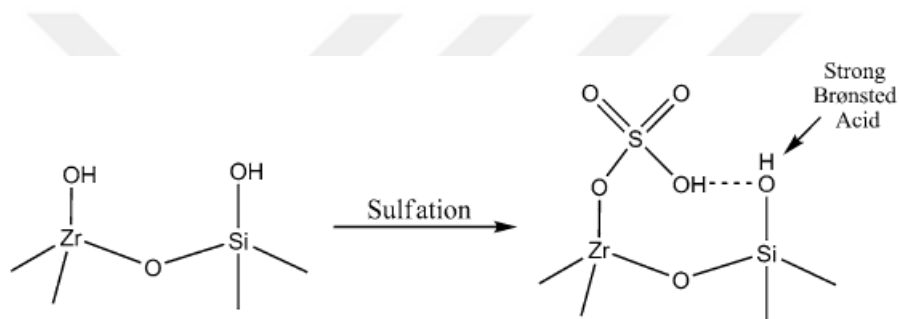


Figure 3.5. Schematic representation of the low coordinated  $Zr^{4+}$  sites and silanol groups on the surface of the Zr-SBA-15 catalysts

(Source: Değirmenci et al., 2010)

### 3.3. Outcomes from Literature Survey

In the literature, molar ratio of reactants, temperature of the reaction, catalyst type, amount of catalyst, the effect of Zr incorporation, hydrophilic-hydrophobic properties of the catalyst, sulfonation of the catalyst, textural properties of the catalyst, acidity amount and types of the catalyst were examined. The results showed the impacts of these parameters on the conversion and yield of the glycosidation reaction.

Homogeneous catalysts such as sulfuric acid were more active and selective for the synthesis of alkyl glucosides. But it was difficult to separate products and they cannot be reused. Enzyme catalysts had also drawbacks such as limitation on operation conditions and low rate of reaction. Because of these reasons, heterogeneous catalysts were much more preferred catalyst types for the glycosidation of alcohol reactions.



The literature studies given above on glycosidation of alcohol reaction provided the following information. Because of the solubility restriction of the glucose in alcohol, excess amount of alcohol should be used in order to avoid mass transfer limitation. The reaction temperature directly affected the glucose conversion and selectivity. While, higher reaction temperature led to side reactions such as oligomerization, below 120° C lower reaction rate was observed. The increase of the catalyst amount positively affected the reaction rate up to 3 wt.%. Metal incorporation into the framework and sulfonation increased the amount and strength of the acidic sites. The amount and strength of Bronsted and Lewis acid sites directly affected the conversion and selectivity. Elemental composition of the catalysts was strongly related to hydrophilic-hydrophobic properties and they affected the adsorption properties of the catalysts. Increase on hydrophilicity of the catalyst led to strong adsorption of glucose, therefore blockage of the pore size and active sites were observed.

In the lights of these studies results, it can be deduced that the best conditions for carrying out the glycosidation reaction is taking the molar ratio of butanol: glucose as 40:1, the mass ratio of glucose: catalyst as 5 and performing the reaction at 117° C.

As catalyst Zr-SBA-15 catalyst and its sulfated form were chosen for glycosidation reaction of butanol. Specifically, required properties of the catalyst for this reaction are high surface area, high amount of acidic sites, large unidirectional cavities and pore windows that restrict the undesired products, well distribution of active metal inside the framework of mesoporous silica material and hydrothermally stability.

## CHAPTER 4

### EXPERIMENTAL STUDY

The aim of the study was to develop heterogeneous catalysts for production butyl glucoside by the glycosidation of butanol. Zr incorporated SBA-15 silica materials with different loading amount of zirconium were synthesized. Zr-SBA-15 catalysts were prepared via hydrothermal synthesis by using gels with two different molar compositions (0.017 P123: 1.0 Si: 0.08 Zr: 220 H<sub>2</sub>O and 0.017 P123: 1.0 Si: 0.1 Zr: 220 H<sub>2</sub>O). Then, they were calcined at 550°C. Sulfated forms of Zr-SBA-15 catalysts were prepared by mixing Zr-SBA-15 with 0.5 M and 1.0 M H<sub>2</sub>SO<sub>4</sub>. After then, they were filtrated, dried and calcined. Lastly, the prepared catalysts (Zr-SBA-15 and SO/Zr-SBA-15) were tested in the reaction.

#### 4.1. Materials

The list of the chemicals used for the experimental study was given in Table 4.1.

Table 4.1. The chemicals used for the experimental study.

Chemicals	Brand / Purity
Pluronic P123	Aldrich average $M_w \sim 5,800$
Zirconium(IV) oxychloride octahydrate	Honeywell $\geq 99.5$
Tetraethyl orthosilicate (TEOS)	Merck 98%
Sulfuric Acid (H <sub>2</sub> SO <sub>4</sub> )	Merck 95%
$\alpha$ -D-Glucose	Aldrich 96%
1-Butanol	Sigma Aldrich 99.8%

#### 4.2. Catalyst Preparation

##### 4.2.1. Preparation of Zr-SBA-15 and Sulfated Zr-SBA-15 Catalysts

Zr-SBA-15 was synthesized for two different Zr contents where the molar ratio of Zr: Si is 0.08: 1.0 and 0.1: 1.0 and they were named as Zr-SBA-15-(0.8) and Zr-SBA-

15-(1.0), respectively. The catalyst preparation procedure was formed based on the study of Değirmenci et al. (Değirmenci et al., 2009).

The amphiphilic copolymer P123 was used as the surfactant. In 150 ml of deionized water, 5 g of P123 was dissolved with continuous stirring at 37°C until the transparent solution was obtained. Besides, in 50 ml of deionized water 1.31 g and 1.63 g zirconium(IV) oxychloride octahydrate was dissolved with continuous stirring at room temperature until the clear solution was obtained. Then, 11.5 ml of TEOS and the aqueous zirconium(IV) oxychloride octahydrate solution was added to the P123 solution. For 24 h, the mixture was stirred at 37°C vigorously. After stirring, the gels were formed with molar compositions of (0.0.17:1.0:0.08:220) and (0.017:1.0:0.1:220) with respect to (P123: Si: Zr: H<sub>2</sub>O). Then the gels were transferred into a Teflon-lined stainless steel autoclave and kept at 100°C for 24 h. The obtained gels, Zr-SBA-15-(0.8) and Zr-SBA-15-(1.0), were centrifuged with an excess amount of deionized water for three times to remove the impurities. After that, the gels were dried overnight at 100°C. Finally, the dried gels were calcined at 550°C for 6 h. During the calcination step, the heating rate to 550 °C was 2°C/min and the cooling rate to 35°C was 5°/min.

In order to prepare 0.5 SO/Zr-SBA-15-(0.8), 1.0 SO/Zr-SBA-15-(0.8), 0.5 SO/Zr-SBA-15-(1.0) and 1.0 SO/Zr-SBA-15-(1.0) catalysts, previously produced Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) were sulfated with 0.5 M and 1.0 M H<sub>2</sub>SO<sub>4</sub>. Firstly, 1 g of Zr-SBA-15-(0.8) was mixed with 15 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> at room temperature for 1 h. This procedure was repeated by using the Zr-SBA-15-(1.0) and sulfated with 0.5 M and 1.0 M sulfuric acid. So, 4 different types of SO-Zr-SBA-15 catalysts were produced. After the filtration, they were dried overnight at 80° C for 12 h. Then, they were calcined at 550° C for 3 h.

### **4.3. Characterization of Catalysts**

The characterization study was carried out in order to investigate the characteristic properties of the prepared catalysts which are Zr-SBA-15-(0.8), Zr-SBA-15-(1.0), 0.5 SO/Zr-SBA-15-(0.8), 1.0 SO/Zr-SBA-15-(0.8), 0.5 SO/Zr-SBA-15-(1.0) and 1.0 SO/Zr-SBA-15-(1.0). In this study, N<sub>2</sub> adsorption, X-Ray diffraction, skeletal FT-IR spectroscopy, X-Ray fluorescence, Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), pyridine adsorbed FT-IR, Thermogravimetric analysis and Scanning

Electron Microscopy (SEM) analyses were also performed. The analysis details are given in the following subheadings.

#### **4.3.1. N<sub>2</sub> Adsorption (BET)**

Micromeritics ASAP 2010 model static volumetric adsorption instrument was used for nitrogen physisorption studies. Prior to adsorption experiments, the catalysts were degassed at 200°C for 2 h. Nitrogen adsorption was carried out at 77 K.

#### **4.3.2. X-Ray Diffraction (XRD)**

Philips X'Pert diffractometer with CuK $\alpha$  radiation was used to determine the crystalline structures of the catalysts. The scattering angle  $2\theta$  was varied between 10° and 80°, with a step length of 0.02.

#### **4.3.3. Skeletal FT-IR Spectroscopy**

In order to analyze the framework vibration of all synthesized catalysts, FTIR spectroscopy was applied. The infrared spectra of the samples were obtained by KBr pellet technique at room temperature. 3 wt. % of the pellets were the samples. Infrared spectrometer type Shimadzu FTIR 8400S was utilized in order to obtain the spectrums in the wavenumber range of 400 - 2000 cm<sup>-1</sup> with resolution of 4 cm<sup>-1</sup>.

#### **4.3.4. Temperature Programmed Desorption of Ammonia**

Temperature-Programmed Desorption of Ammonia (NH<sub>3</sub>-TPD) method was applied by Micromeritics AutoChem II Chemisorption Analyzer instrument, in order to determine the acidity of the catalysts. Up to 400 °C, the catalyst samples were heated with 5 °C/min heating rate. Then, for 30 minutes they were kept at this temperature under He gas flow (70 ml/min). After that, the sample was cooled to 60 °C at a rate of 5 °C/min under He gas flow (30 ml/min). Then the flow was switched to NH<sub>3</sub>-He gas mixture (30 ml/min) for 30 min. The sample was degassed for 2 h at 60 °C under He flow (70 ml/min) in order to remove physically adsorbed ammonia. The sample was heated from 60 °C to 700 °C with 10 °C/min heating rate, in order to analyze the desorption pattern of ammonia from the sample. The measurements of thermal conductivity detector were recorded.

#### **4.3.5. X-Ray Fluorescence (XRF)**

X-Ray Fluorescence technique was used in order to analyze the elemental composition of the catalysts. By using Spectro IQ II instrument and CuK $\alpha$  radiation, the analyses were carried out with powder method.

#### **4.3.6. Pyridine Adsorbed FT-IR**

Pyridine adsorption/desorption method was applied to determine Bronsted and Lewis acidity characteristics of the catalysts by using IR spectroscopy. For 2 h, vacuum was applied to the samples at 300 °C in order to activate the samples. Pyridine adsorption was performed at 150 °C for 30 min. For 2 h, the samples were kept at 120 °C under N<sub>2</sub> flow (30 ml/min) so as to desorb the physisorbed pyridine. Using KBr pellet technique, Shimadzu FT-IR 8400s model FT-IR Spectrometer were utilized in order to perform IR analyses between 400 and 4000 cm<sup>-1</sup>. The mixture of 150 mg KBr and 2 mg of pyridine adsorbed catalyst sample was pressed, thus the pellets were prepared.

#### **4.3.7. Thermogravimetric Analysis (TGA)**

TGA analyzes were performed under dry air with 5°C/min heating rate in Shimadzu TGA-51 device up to 1000°C.

#### **4.3.8. Scanning Electron Microscopy (SEM)**

Philips XL 30S FEG scanning electron microscopy was used to visualize of the morphology of the catalysts.

### **4.4. Synthesis of Butyl Glucoside**

The production of butyl glucoside with acetalization reaction of glucose with n-butanol was carried out for 6 different catalysts (Zr-SBA-15-(0.8), Zr-SBA-15-(1.0), 0.5 SO/Zr-SBA-15-(0.8), 0.5 SO/Zr-SBA-15-(1.0), 1.0 SO/Zr-SBA-15-(0.8) and 1.0 SO/Zr-SBA-15-(1.0)).

The amount of reactants and catalyst were determined by taking the molar ratio of n-butanol: glucose as 40:1 and the mass ratio of glucose: catalyst as 5. The reaction

system consisted of reaction station, two necked round-bottom glass flask (100 ml) and a Teflon coated magnetic stirring bar as shown in Figure 4.1.

Firstly, 100 ml round-bottom glass flask equipped with a condenser was placed in the reaction station which heats, stirs and refluxes multiple samples under an inert atmosphere (Figure 4.1). Nitrogen flow into the reactor was set to 40 ml/min. Then, 50 ml butanol was added into the flask and heated up to 117° C. After reaching 117° C, 0.5 g catalyst and 2.5 g glucose were added into the reactor successively. Magnetic stirrer was adjusted to 1000 rpm. After then, the reaction mixture was allowed at 117° C, under nitrogen atmosphere for 6 h. During the reaction, samples (0,5 ml) were taken into a vial in every hour in order to analyze the products later. Then, until the product analysis these samples were kept in the refrigerator.

For the comparison purposes, the reaction tests were also performed with no catalyst and sulfuric acid in the same reaction conditions. 5 µl H<sub>2</sub>SO<sub>4</sub> was added as homogeneous catalyst in order to carry out the reaction.



Figure 4.1. The reactor set-up

#### 4.5. Product Analysis

Before the analysis, the samples were centrifuged and filtered. Thus, the remaining of the catalyst and impurities were removed from the samples. Product analysis of the reaction samples were performed with Agilent 1100 Series HPLC. For analysis Thermo Hyperez (30 cm \* 0.77 cm) column was used. Analysis were performed at 50°C

by 3mM H<sub>2</sub>SO<sub>4</sub>. Flow rate of the mobile phase was 3 mmol/min. For quantification of the products, calibration curve of the products was obtained by using the standard of butyl glucopyranoside. The calibration curve of the products was given in Figure 4.2. Lastly, the concentration of butyl glucofuranoside and butyl glucopyranoside were calculated.

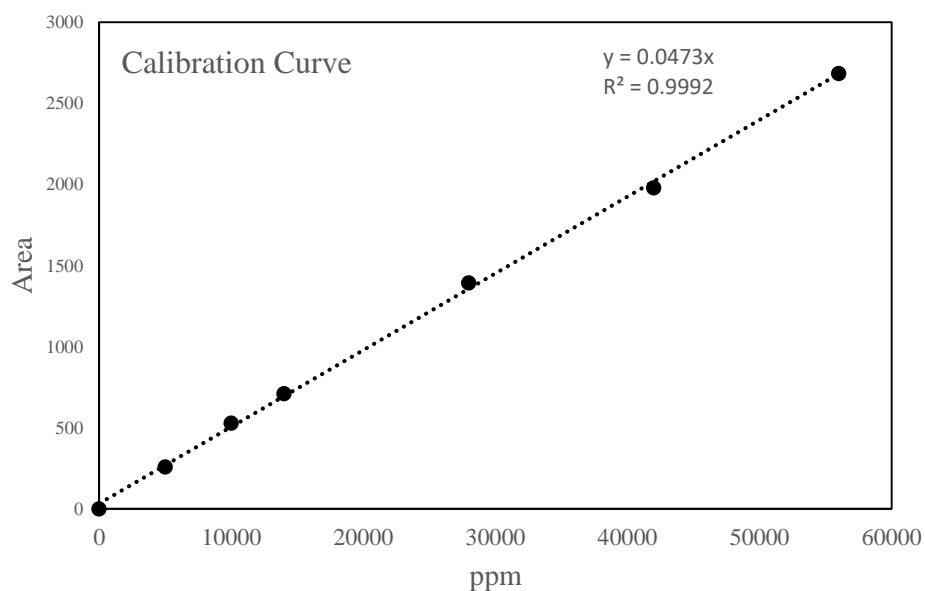


Figure 4.2. HPLC calibration curve for butyl glucosides

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1. Characterization of the Catalysts

The crystal structure of catalysts was investigated with X-ray diffraction by changing  $2\theta$  angles from  $10^\circ$  to  $80^\circ$  and the results are given in Figure 5.1. The higher peaks close to  $25^\circ$  refer that Zr was successfully incorporated in SBA-15 structure. Also absence of characteristic peaks belonging to Zr proved the dispersion of Zr compounds in SBA-15. Nonexistence of peaks that are related to crystalline phase in high angle region indicates that either zirconia particles are very small to give any diffraction or zirconium atoms coated on the pore walls are amorphous (Fuxiang et al., 2007; Değirmenci et al., 2010).

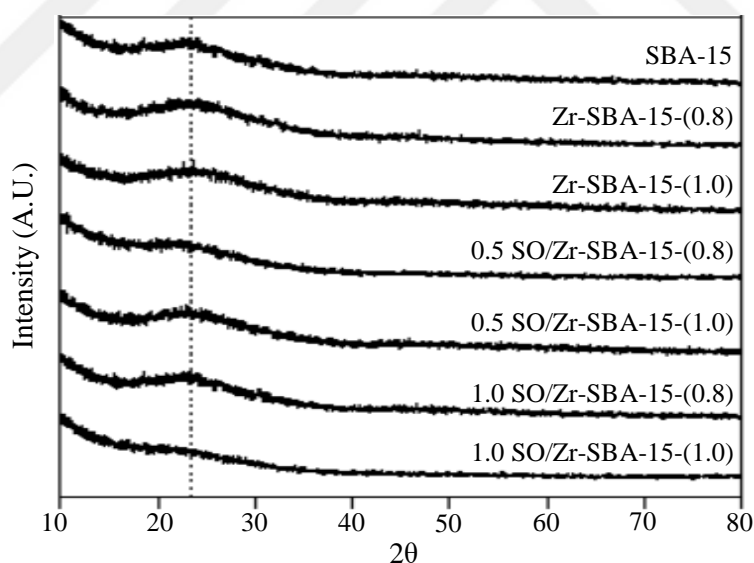


Figure 5.1. XRD patterns of the catalysts

Zirconia was mainly located inside the pores of SBA-15. Therefore, growing into the larger crystals was restrained. Hydrothermal stability of the catalyst cannot be observed if zirconia particles primarily exist outside the pores. Even at high calcination temperature, the zirconia particles noncrystallize because of the strength of interaction between zirconia and silica surface. According to the results, XRD patterns of the sulfated



forms of Zr-SBA-15 were similar to their parent forms. Then, it can be concluded from that the structure was preserved after sulfonation process (Krishnan et al., 2008).

X-Ray Fluorescence was used in order to find out the elemental composition of the catalysts. Zr/Si and S/Zr ratio of the catalysts were calculated according to the results obtained from the XRF analysis as given in Table 5.1. The ratio of the amount of zirconium added to the synthesis gel and the amount of zirconium contents in catalyst after the calcination was close to each other which indicated the efficiency of incorporation of zirconium. Zr-SBA-15-(0.8) with 0.075 ratio slightly lower than the synthesis mixture (Zr/Si: 0.08). As opposed to this, Zr-SBA-15-(1.0) with 0.113 ratio was slightly higher than the synthesis mixture (Zr/Si: 0.1). Zr/Si ratio increased by the Zr loading and slightly decreased by the sulfonation. The results implied that after sulfonation process, Zr-SBA-15-(0.8) had more sulfur content comparing to the Zr-SBA-15-(1.0) catalyst. Also, sulfonation with increased amount of sulfate lead fractional increase to the S/Zr ratio.

Table 5.1. Textural properties and acidities of the prepared catalysts

Catalyst	BET Surface Area, m <sup>2</sup> /g	Pore Volume, cm <sup>3</sup> /g	Pore Diameter, A	Zr/Si	S/Zr	Total Acidity <sup>a</sup>	B/L <sup>b</sup>
SBA-15	773.1	1.18	44.7	-	-	0.04	-
Zr-SBA-15-(0.8)	741.6	0.747	45.55	0.075	-	1.18	1.12
Zr-SBA-15-(1.0)	655.9	0.459	30.39	0.113	-	1.36	0.84
0.5 SO/Zr-SBA-15-(0.8)	466.2	0.484	39.59	0.072	0.282	1.65	1.27
0.5 SO/Zr-SBA-15-(1.0)	424.2	0.273	29.37	0.083	0.082	1.74	1.12
1.0 SO/Zr-SBA-15-(0.8)	461.7	0.500	41.66	0.069	0.297	2.24	1.18
1.0 SO/Zr-SBA-15-(1.0)	435.0	0.350	28.17	0.078	0.181	2.35	1.97

<sup>a</sup>Total Acidity (mmol NH<sub>3</sub>/g cat.)

<sup>b</sup>The ratio of Bronsted to Lewis acid sites peak areas

The sulfur leaching from the catalyst was investigated by the elemental analysis of fresh and used 1.0 SO/Zr-SBA-15-(1.0) catalysts. Table 5.2 shows S and SO<sub>3</sub> contents in 1.0 SO/Zr-SBA-15-(1.0) catalyst. According to the results, the amount of sulfur within the catalyst decreased around 9 wt.%. This was attributed to sulfur leaching from the catalyst during the glycosidation reaction. Strong support-metal-sulfur interaction can prevent sulfur leaching (Yang et al., 2003).

Table 5.2. S and SO<sub>3</sub> contents of fresh and used 1.0 SO/Zr-SBA-15-(1.0) catalyst

	S (wt.%)	SO <sub>3</sub> (wt.%)
Fresh	3.38	4.43
Used Catalyst	3.07	4.02

N<sub>2</sub> adsorption isotherms of Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) and their sulfated forms are given in Figure 5.2, Figure 5.3 and Figure 5.4. Adsorption on mesoporous solids proceeds via multilayer adsorption followed by capillary condensation. According to the characteristic features of isotherms, their hysteresis loops proved that the capillary condensation take place in mesoporous. The adsorption isotherms of type IV indicated that Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) and their sulfated versions have mesoporous structure.

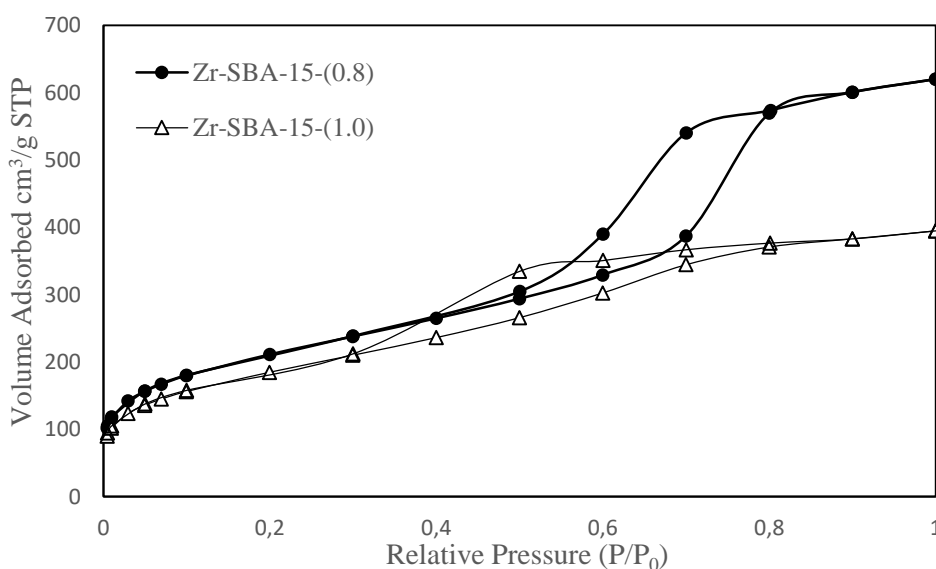


Figure 5.2. N<sub>2</sub> adsorption/desorption isotherm of Zr-SBA-15 catalysts

Surface area, pore volume and pore diameter of Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) and their sulfated forms are given in Table 5.1. N<sub>2</sub> adsorption was applied in order to obtain the values of BET surface area, pore volume and pore diameter of the catalysts. The results showed that surface area decreased by the increase of the Zr incorporation into the framework and sulfonation process. The surface area of Zr-SBA-15 was 741.6 m<sup>2</sup>/g and this value was decreased significantly up to 424.2 m<sup>2</sup>/g after Zr loading and sulfonation carried out.

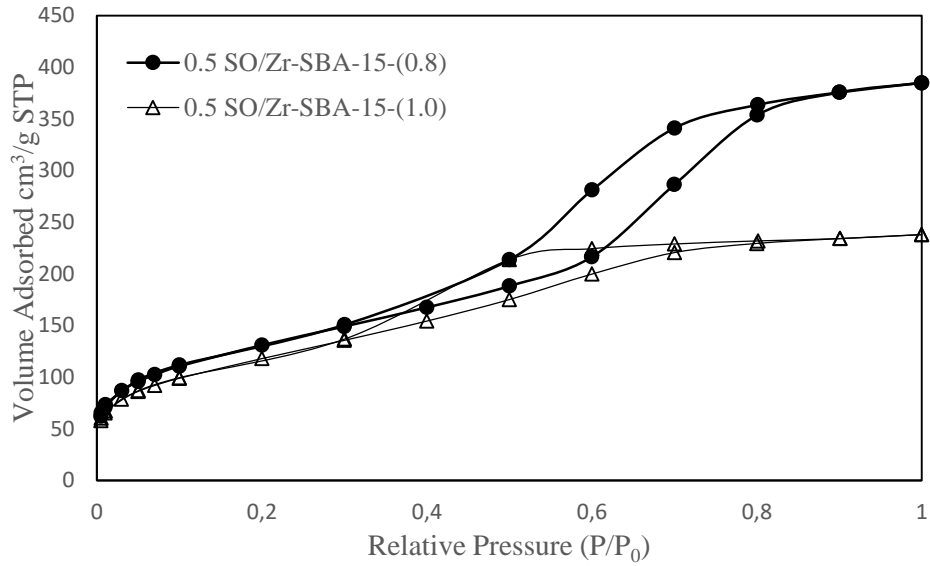


Figure 5.3. N<sub>2</sub> adsorption/desorption isotherm of 0.5 SO/Zr-SBA-15 catalysts

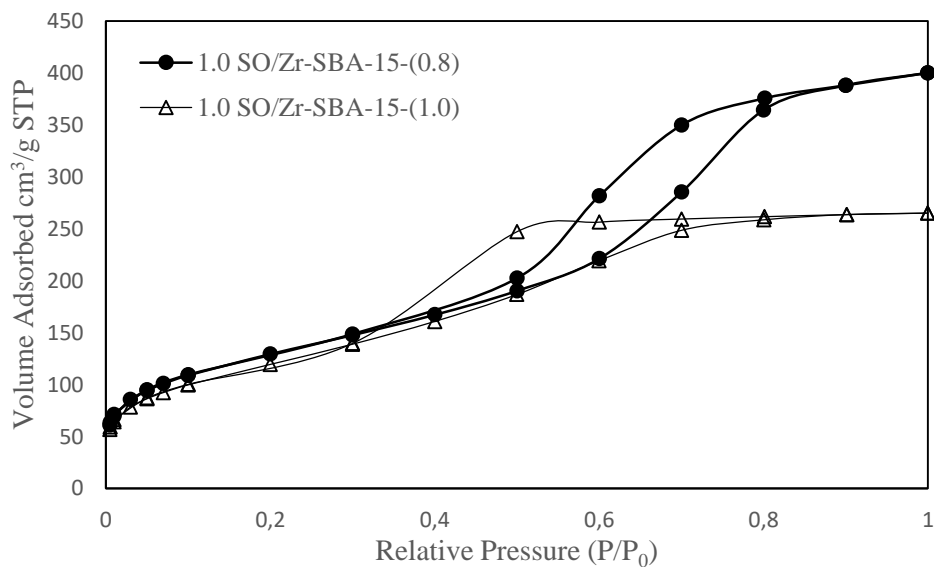


Figure 5.4. N<sub>2</sub> adsorption/desorption isotherm of 1.0 SO/Zr-SBA-15 catalysts

According to the textural properties of the catalysts, incorporation of the zirconium in large quantities reduced the surface area and pore volume. When zirconium loading was increased into the catalyst structure, adsorption isotherms detected pore volume loss. It also indicated that zirconium incorporation into the catalyst could lead blockage of the micropores (Iglesias et al., 2011). Pore volume of the catalyst were decreased by the Zr loading. When sulfonation applied Zr-SBA-15 catalyst pore volume decreased. On the other hand, increasing the amount of sulfate slightly increased the pore

volume of the catalysts. According to the results, pore diameter decreased by the Zr loading. But after sulfated, barely decrease was observed.

The acidity of the catalysts was determined by calculating the area under the NH<sub>3</sub>-TPD profiles (Table 5.1). The NH<sub>3</sub>-TPD profiles of the catalysts are shown in Figure 5.5. The desorption peaks of catalysts were widely spread and the temperature ranged from 100°C to 500°C. Accordingly, it can be concluded that all Zr-SBA-15 based catalysts have weak, medium and strong acid sites. When the TPD results of Zr-SBA-15 catalysts with and without sulfates were compared, it was noted that the sulfonation process increased the acidity of the catalyst.

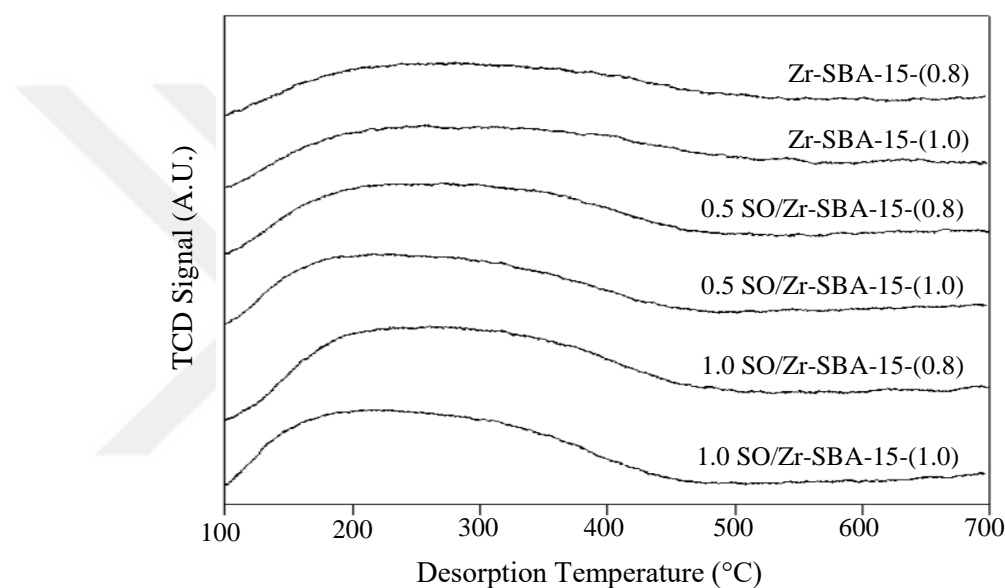


Figure 5.5. NH<sub>3</sub>-TPD profile of the prepared catalysts

Total acidity of the catalysts increased by Zr loading and sulfonation (Table 5.1). While 1.0 SO/Zr-SBA-15-(1.0) catalyst provided the highest acidity (2.35 mmol NH<sub>3</sub>/g cat.), Zr-SBA-15-(0.8) catalyst provided the lowest acidity (1.18 mmol NH<sub>3</sub>/g cat.).

The skeletal FT-IR spectra of the catalysts are given in Figure 5.6. The peaks at 1053 cm<sup>-1</sup> and 1220 cm<sup>-1</sup> were related to the symmetric stretching of Si-O-Si bonds. Moreover, a peak was observed at 418 cm<sup>-1</sup> due to the vibration of Si-O-Si bond. The incorporation of Zr on the SBA-15 formed the Si-O-Zr bond and it was observed at 966 cm<sup>-1</sup>. The existence of this band proved the incorporation of Zr in SBA-15. Also, FT-IR spectra of the sulfated catalysts had similar peaks with their parent forms and this indicated that sulfonation did not change the structure of the catalysts. Therefore, it can

be concluded that Zr-SBA-15-(0.8) and Zr-SBA-15-(1.0) catalysts and their sulfated forms were successfully produced. (Liang et al., 2010)

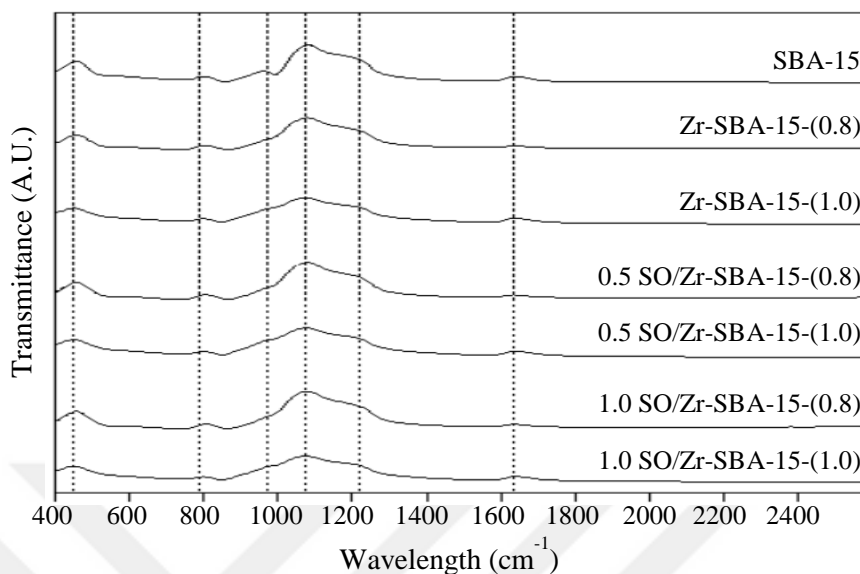


Figure 5.6. Skeletal FT-IR spectra of the prepared catalysts

The spectra of pyridine adsorbed catalysts were examined to characterize the acid sites of the catalysts. The FT-IR spectrums of pyridine adsorbed Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) and their sulfated forms are given in Figure 5.7. Three peaks were detected for all of the catalysts. The peaks at  $1455\text{ cm}^{-1}$  and  $1540\text{ cm}^{-1}$  indicate Lewis and Bronsted acid sites respectively. On the other hand, the peak at  $1490\text{ cm}^{-1}$  refers both Lewis and Bronsted acid sites. Higher peaks represent higher amount of acidity and the highest peak belonged to 1.0 SO/Zr-SBA-15-(1.0) catalyst. The ratio of Bronsted to Lewis acid sites were calculated from the areas under the peaks at  $1540\text{ cm}^{-1}$  and  $1455\text{ cm}^{-1}$ . The ratio of Bronsted to Lewis acid sites peak areas are also given in Table 5.1. The highest B/L ratio (1.97) was obtained with 1.0 SO/Zr-SBA-15-(1.0), whereas the lowest B/L ratio (1.12) was obtained with Zr-SBA-15-(1.0). According to the results, sulfated catalysts had similar FT-IR spectra with their parent forms. This referred that the structure of the catalysts was retained (Hoo et al., 2014).

Thermal gravimetric analysis of the catalysts are given in Figure 5.8. A sharp weight loss was observed up to  $150^{\circ}\text{C}$  which was attributed to the desorption of adsorbed water molecules. Within the temperature range of  $150^{\circ}\text{-}550^{\circ}\text{C}$ , another weight loss region was observed. Removal of organic molecule residues such as P123 residing in SBA-15 could be the reason of this loss. The sulfated forms of Zr-SBA-15 showed

another weight loss above 600° C and it was related to the decomposition of the sulfates. According to these results, sulfates were stable up to 600° C.

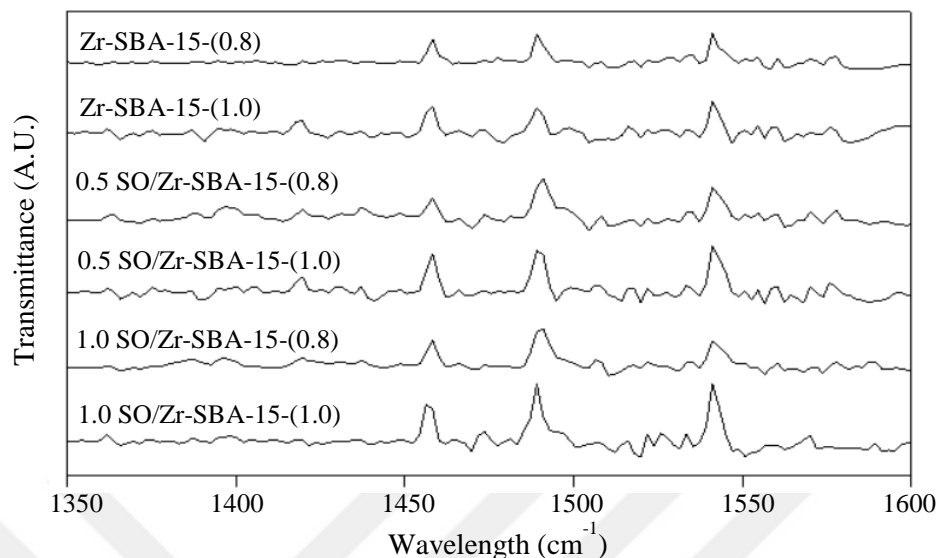


Figure 5.7. FT-IR spectra of pyridine adsorbed catalysts

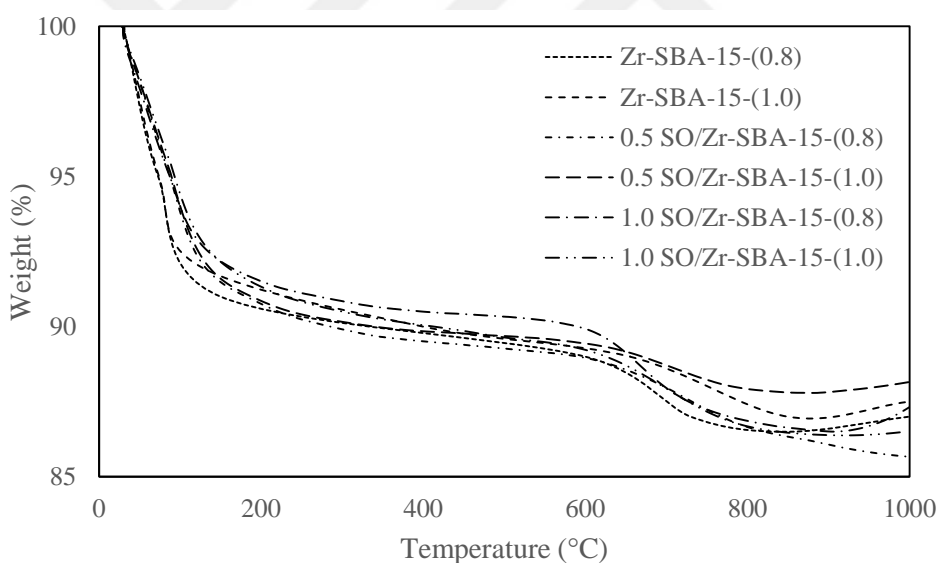
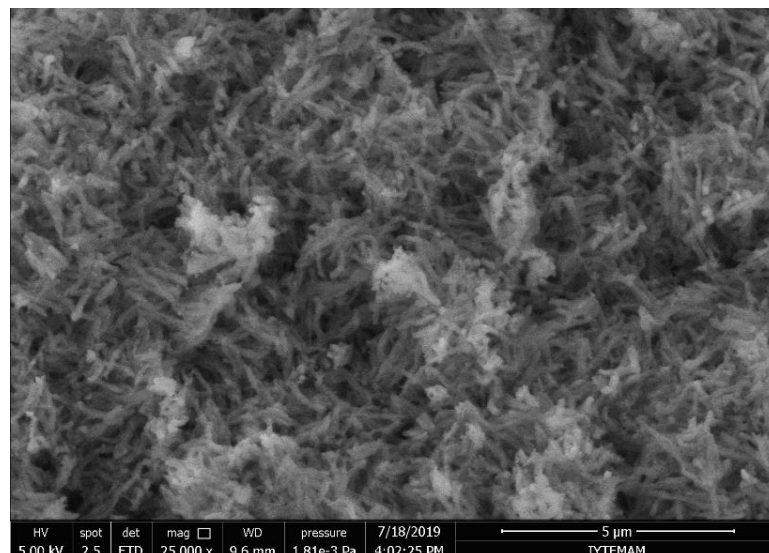


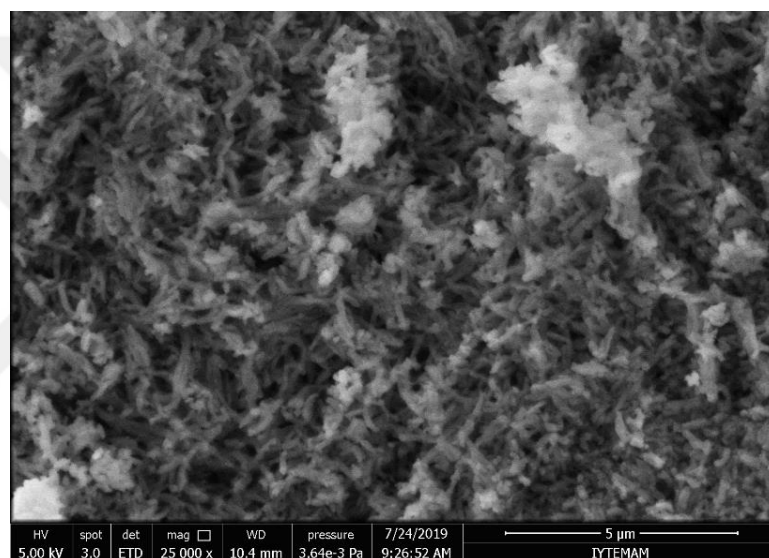
Figure 5.8. TGA graphs of the prepared catalysts

SEM micrographs of Zr incorporated SBA-15 catalysts and their sulfated forms are demonstrated in Figure 5.9 and Figure 5.10. The darker zones can be assigned to silica rich surfaces, whereas the lighter zones correspond to zirconia rich surfaces. Accordingly, it was observed that Zr-SBA-15-(0.8) catalyst had wheat-like particles which was similar to the SBA-15. On the other hand, morphology of the other catalysts changed by increasing amount of zirconium and sulfonation (Qin et al., 2013; Ogura et al., 2016).

a)



b)



c)

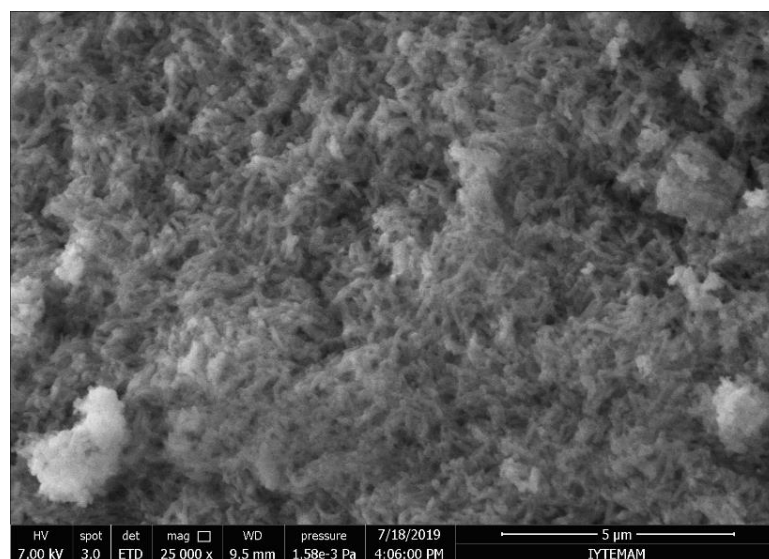
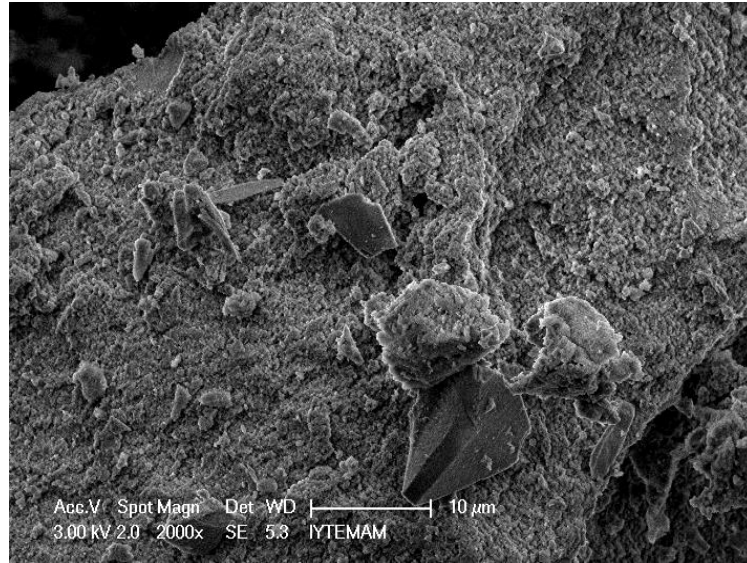


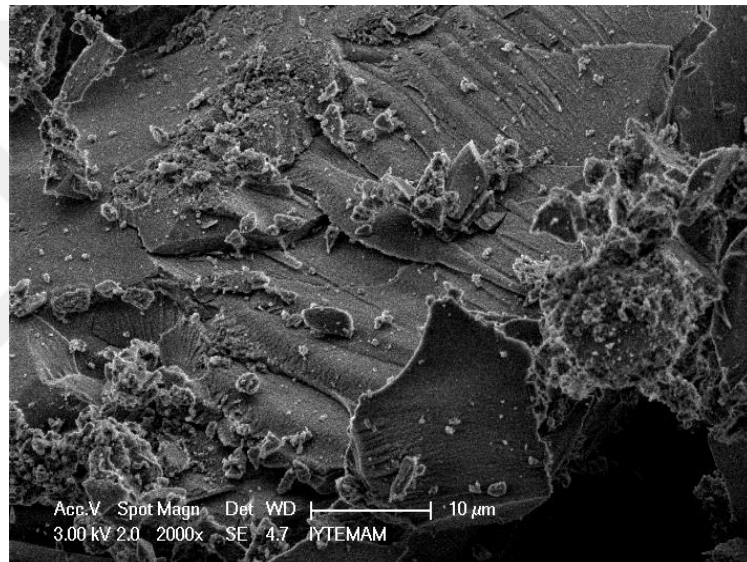
Figure 5.9. Scanning electron micrographs

a) Zr-SBA-15-(0.8) b) 0.5 SO/Zr-SBA-15-(0.8) c) 1.0 SO/Zr-SBA-15-(0.8) magnification 25000x

a)



b)



c)

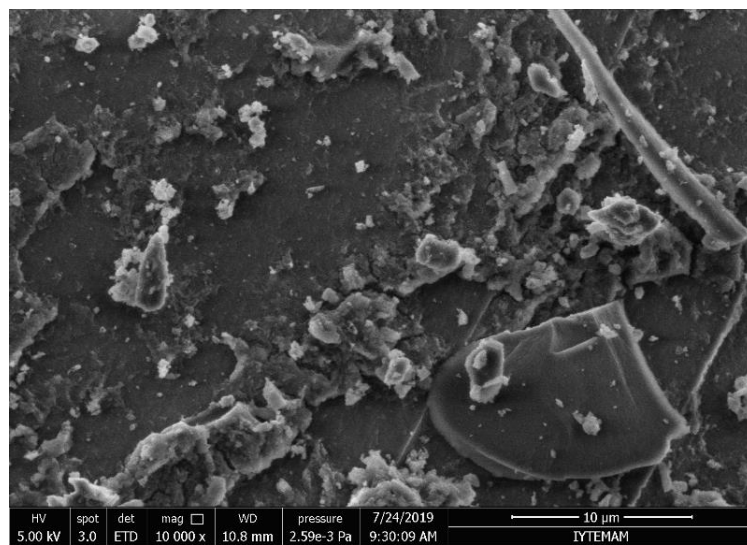


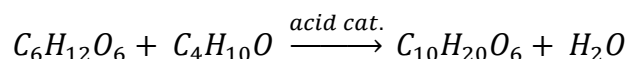
Figure 5.10. Scanning electron micrographs

a) Zr-SBA-15-(1.0) b) 0.5 SO/Zr-SBA-15-(1.0) c) 1.0 SO/Zr-SBA-15-(1.0) magnification 2000-10000x



## 5.2. Catalysts Testing in Synthesis of Butyl Glucosides

Under the same reaction conditions, the reaction tests were carried out with homogeneous and heterogeneous catalysts. The effect of sulfonation on the catalyst activity was investigated. Consequently, the effects of the catalyst properties such as surface area, pore volume, pore diameter, acidity and elemental composition were discussed. In this reaction excess amount of butanol was used due to the solubility restriction of the glucose in butanol. Glycosidation of butanol is given below.



1 mol glucose reacts with 1 mol butanol over an acidic catalyst and 1 mol butyl glucoside is produced. Water is also formed as side product in this reaction. Since butyl glucofuranoside (BGF) and butyl glucopyranoside (BGP) are the isomers of butyl glucoside, sum of moles of these isomers give the number of mol glucose converted in this reaction. Butyl glucoside yield was calculated using Eqn 5.1.

$$Yield = \frac{[P]}{[R_{in}]} \quad \text{Eqn. (5.1.)}$$

[P]: Number of moles of the product (butyl glucofuranoside and butyl glucopyranoside)

[R<sub>in</sub>]: Number of moles of the reactant (glucose) fed into the reactor

Product analysis of the reaction samples were performed with HPLC. In Figure 5.11 and Figure 5.12, HPLC chromatograms of the samples taken after the reaction with homogeneous (H<sub>2</sub>SO<sub>4</sub>) and heterogeneous (1.0 SO/Zr-SBA-25-(1.0)) catalysts are given respectively. The peak at 19 min indicates glucose and the figures showed that the concentration of glucose decreased as the reaction progressed. The peaks at 26 and 29 min indicate butyl glucofuranoside and butyl glucopyranoside respectively. The amount of the butyl glucofuranoside and butyl glucopyranoside increased with reaction time.

The first reaction test was performed with no catalyst. The results showed that only 1.2 % yield of butyl glucofuranoside was obtained. The production of butyl glucopyranoside was not observed. It proved the fact that acidic catalyst is necessary for synthesize butyl glucoside.

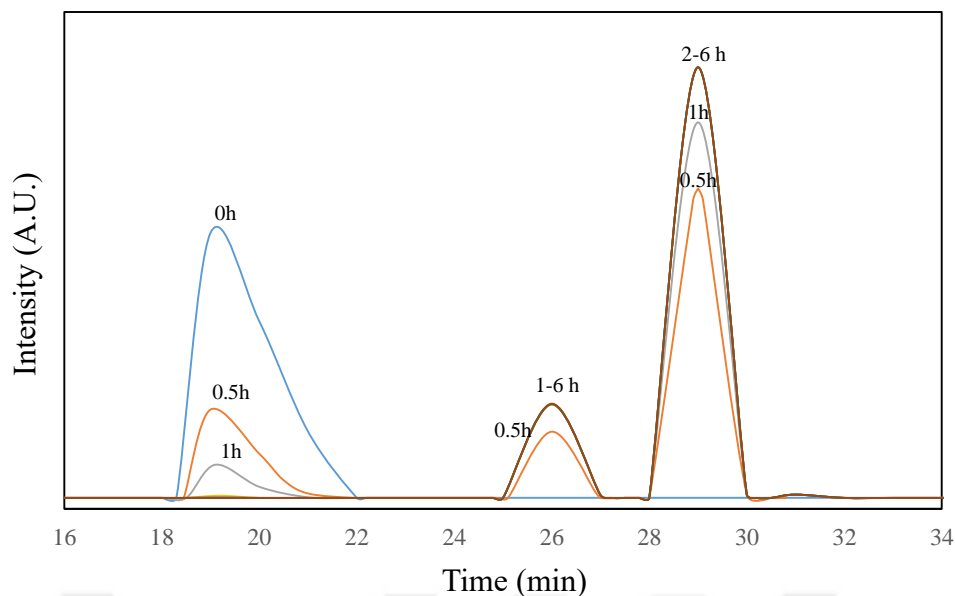


Figure 5.11. HPLC chromatograms of the samples taken after the reaction carried out with homogeneous ( $\text{H}_2\text{SO}_4$ ) catalyst

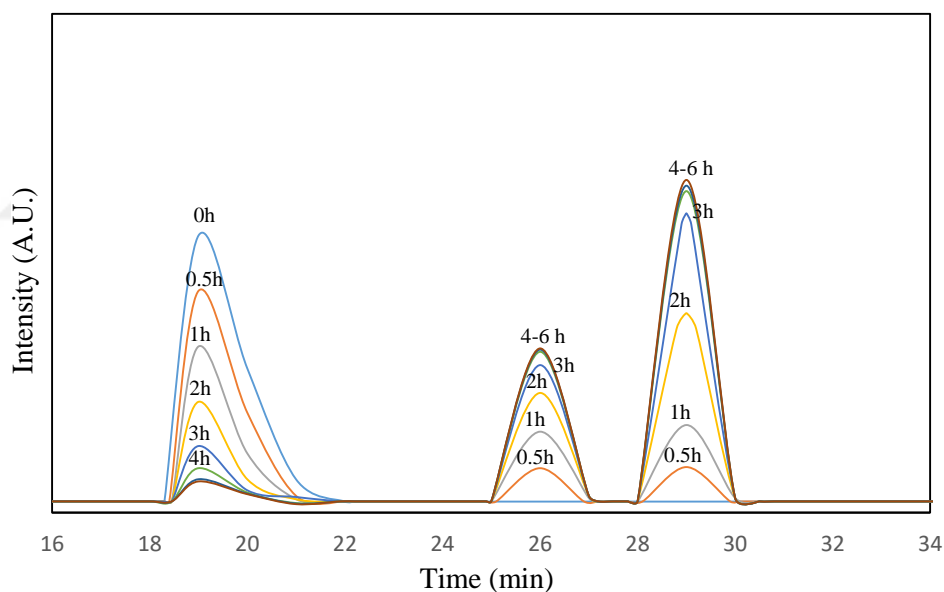


Figure 5.12. HPLC chromatograms of the samples taken after the reaction carried out with heterogeneous ( $1.0 \text{ SO/Zr-SBA-15-(1.0)}$ ) catalyst

In order to evaluate the difference between homogeneous and heterogeneous catalyst, sulfuric acid was selected and used as homogeneous catalyst in glycosidation reaction of butanol. The results showed that glucose was completely converted into the butyl glucoside after 2 h of the reaction (Figure 5.13). Butyl glucofuranoside and butyl glucopyranoside were the products obtained. Butyl glucopyranoside was formed much higher amounts (79%) than butyl glucofuranoside (21%).

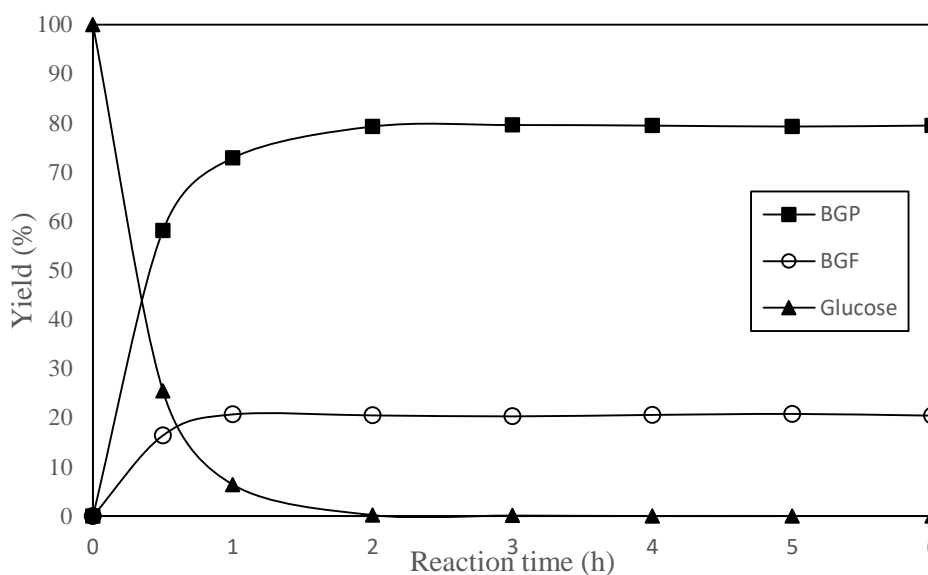


Figure 5.13. The conversion of glucose with H<sub>2</sub>SO<sub>4</sub> catalyst with respect to time

The first reaction tests over heterogeneous catalysts were carried out with Zr-SBA-15-(0.8) and Zr-SBA-15-(1.0). The yield change with respect to time are given in Figure 5.14 and Figure 5.15. It was observed merely conversion of glucose; hence the yield of butyl glucosides was very low. Zr-SBA-15-(0.8) provided slightly higher butyl glucoside yield (9%) than Zr-SBA-15-(1.0). It was related to higher B/L ratio of Zr-SBA-15-(0.8). Since, Bronsted acid sites were the active sites for the glycosidation reaction of butanol.

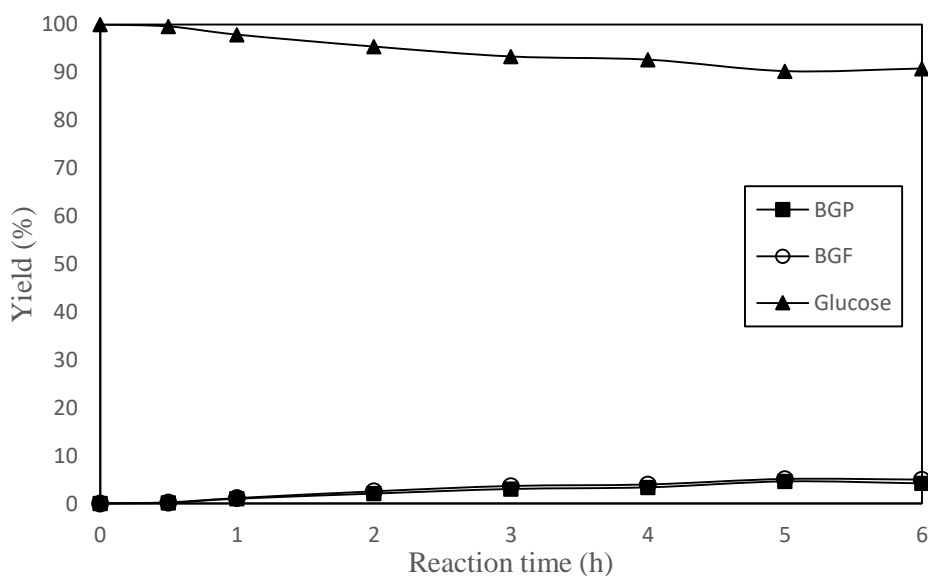


Figure 5.14. The conversion of glucose with Zr-SBA-15-(0.8) catalyst with respect to time

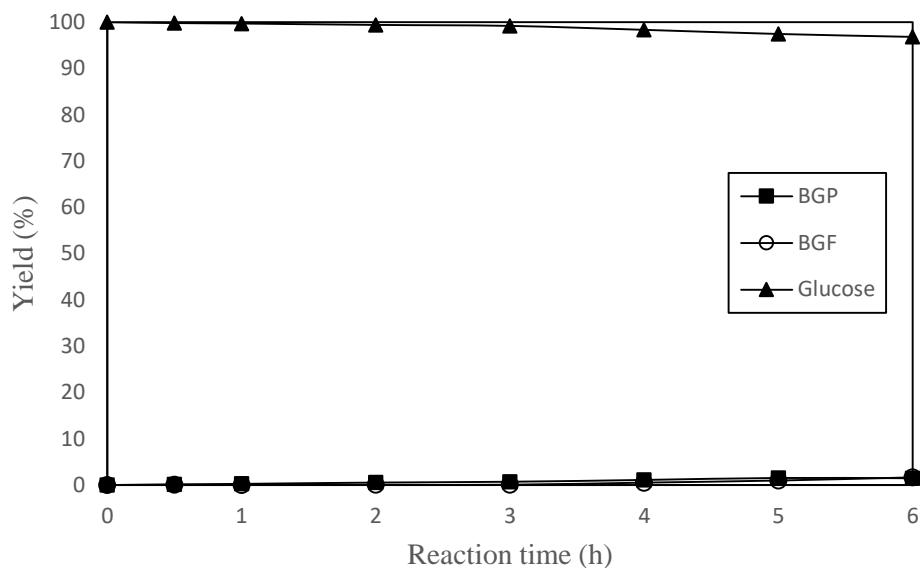


Figure 5.15. The conversion of glucose with Zr-SBA-15-(1.0) catalyst according to time

Zr-SBA-15-(0.8) and Zr-SBA-15-(1.0), which were sulfated with 0.5M H<sub>2</sub>SO<sub>4</sub>, were transformed into 0.5 SO/Zr-SBA-15-(0.8) and 0.5 SO/Zr-SBA-15-(1.0). As illustrated in Figure 5.16 and Figure 5.17, butyl glucoside yield (80%) obtained by 0.5 SO/Zr-SBA-15-(0.8), was almost same as the yield (83%) obtained by 0.5 SO/Zr-SBA-15-(1.0). But, pyranoside/furanoside ratio was favored by 0.5 SO/Zr-SBA-15-(0.8). This can be attributed to higher Bronsted/Lewis acid sites ratio of this catalyst. Sulfated form of the catalysts showed much better yields and this was attributed to increased acid sites on the sulfated form of the catalysts.

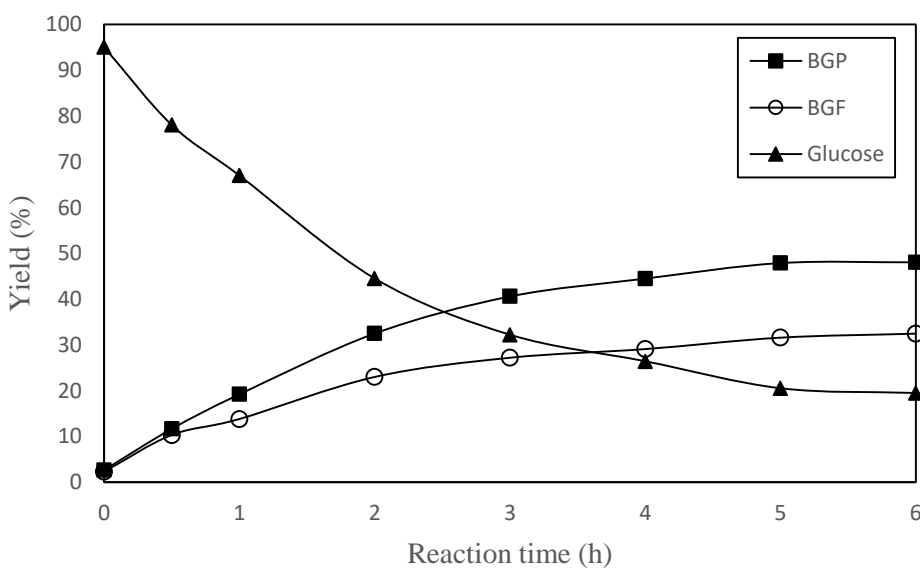


Figure 5.16. The conversion of glucose with 0.5 SO/Zr-SBA-15-(0.8) catalyst with respect to time

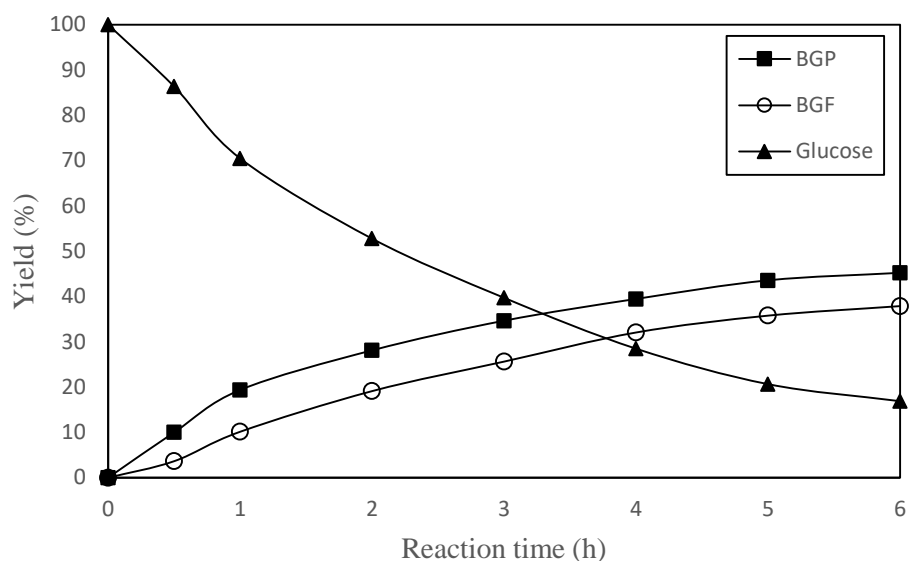


Figure 5.17. The conversion of glucose with 0.5 SO/Zr-SBA-15-(1.0) catalyst with respect to time

1.0 SO/Zr-SBA-15-(0.8) and 1.0 SO/Zr-SBA-15-(1.0) catalysts were tested in glycosidation reaction of butanol. As illustrated in Figure 5.18 and Figure 5.19, total butyl glucoside yield increased up to 92% by 1.0 SO/Zr-SBA-15-(1.0). The amount of butyl glucopyranoside yield (60%) was almost two times the amount of butyl glucofuranoside yield (31%). Also, almost the same product yields (90%) were obtained by 1.0 SO/Zr-SBA-15-(0.8). Comparing to 0.5 SO/Zr-SBA-15 catalysts, conversion of glucose and yield of butyl glucopyranoside were observed to be slightly higher for 1.0 SO/Zr-SBA-15-(0.8). This can be attributed to the higher acidity and B/L ratio of the catalysts.

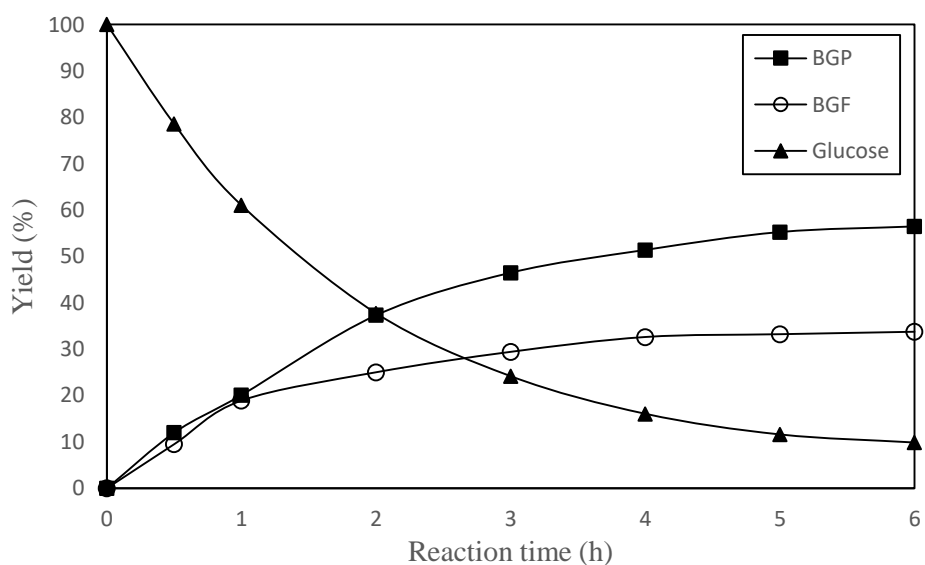


Figure 5.18. The conversion of glucose with 1.0 SO/Zr-SBA-15-(0.8) catalyst with respect to time

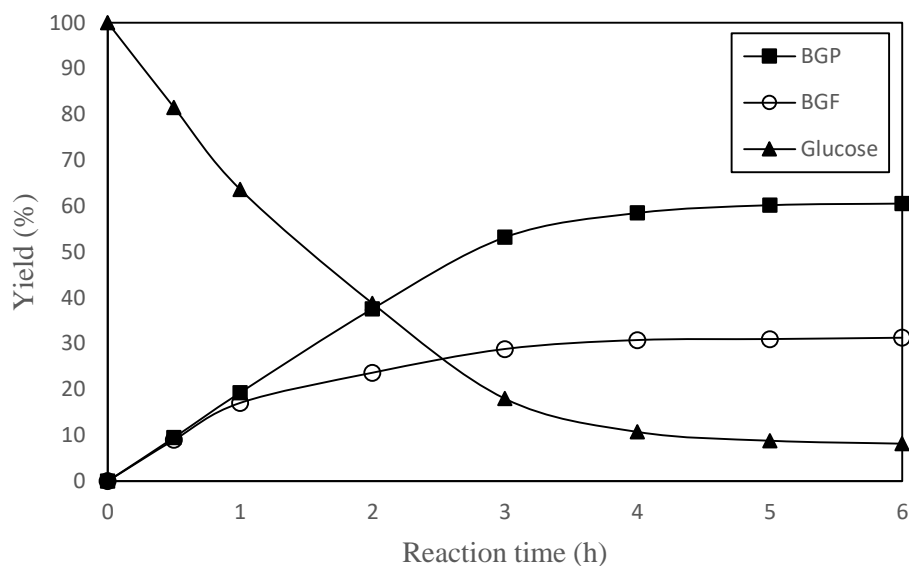


Figure 5.19. The conversion of glucose with 1.0 SO/Zr-SBA-15-(1.0) catalyst with respect to time

The results of the activity tests of the catalysts are compared in Figure 5.20. Zr-SBA-15-(0.8) and Zr-SBA-15-(1.0) catalysts were found to have low activity in the reactions. The catalysts were more active, after sulfonation process.

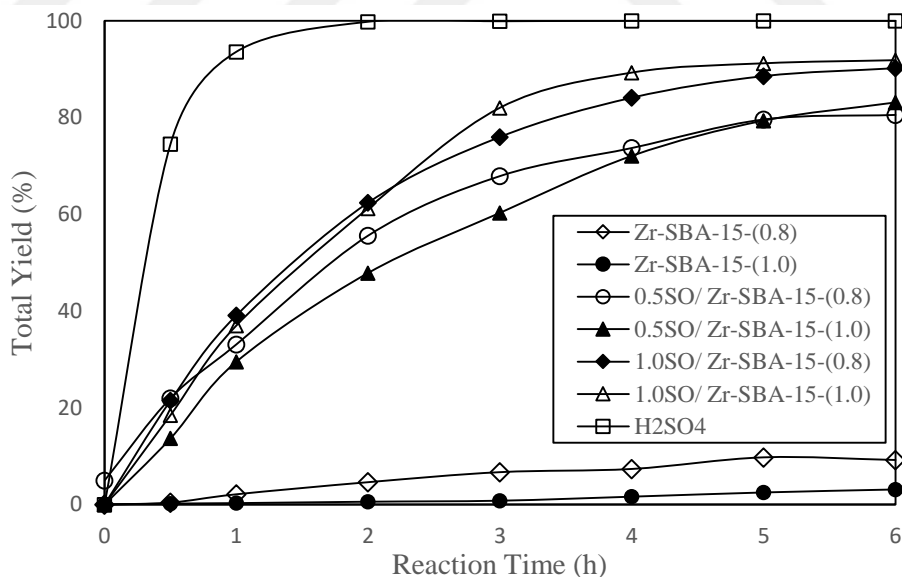


Figure 5.20. Butyl glucoside yield by H<sub>2</sub>SO<sub>4</sub>, Zr-SBA-15 and its sulfated forms

The yield of the products that obtained after glycosidation reaction by different catalysts are given in Table 5.3. 1.0 SO/Zr-SBA-15-(1.0) showed the best catalytic activity (92 %) in the glycosidation reaction. This result could be attributed to the highest acidity and B/L ratio of this catalyst. Consequently, it can be deduced that sulfated form

of zirconium incorporated silica based SBA-15 mesoporous catalyst is a good alternative to the homogeneous catalysts.

Table 5.3. Butyl glucoside yields obtained over the catalysts studied

Catalyst	Butyl glucofuranoside (%)	Butyl glucopyranoside (%)	Total Yield (%)
No catalyst	1.2	0	1.2
H <sub>2</sub> SO <sub>4</sub>	20.4	79.5	99.9
Zr-SBA-15-(0.8)	5.0	4.2	9.2
Zr-SBA-15-(1.0)	1.6	1.5	3.1
0.5SO/ Zr-SBA-15-(0.8)	32.5	48.1	80.5
0.5SO/ Zr-SBA-15-(1.0)	37.9	45.2	83.1
1.0SO/ Zr-SBA-15-(0.8)	33.7	56.4	90.1
1.0SO/ Zr-SBA-15-(1.0)	31.4	60.6	92.0

The reusability of the catalysts was determined by testing 1.0 SO/Zr-SBA-15-(1.0) catalyst in the reaction. The yield of the butyl glucofuranoside, butyl glucopyranoside and total yield over fresh and used catalysts are presented in Table 5.4. The total butyl glucoside yield obtained over 1.0 SO/Zr-SBA-15-(1.0) catalyst decreased about 7% after the reusability test. This was determined to be due to the sulfur leaching from the catalyst.

Table 5.4. The reusability tests of 1.0 SO/Zr-SBA-15-(1.0) catalyst

Catalyst	Butyl glucofuranoside (%)	Butyl glucopyranoside (%)	Total Yield (%)
Fresh	31.4	60.6	92
1 <sup>st</sup> reuse	29.7	56.1	85.8
2 <sup>nd</sup> reuse	27.7	52.5	80.2

## CHAPTER 6

### CONCLUSION

Zr-SBA-15 catalysts with different amount of zirconium loadings (Zr/Si: 0.08 and 0.1) were synthesized. Zirconium was successfully incorporated into the SBA-15 framework. By zirconium loading and sulfonation; surface area, pore volume, pore diameter, acidity and elemental composition of the catalysts were changed. Pore diameter was decreased by the loading of zirconium. Acidity was increased by zirconium loading and sulfonation. All catalysts had mesoporous structure and their structure were preserved after sulfonation.

Zr-SBA-15-(0.8), Zr-SBA-15-(1.0) and their sulfated forms (0.5 SO and 1.0 SO) were used as catalyst in glycosidation reaction of butanol. Butyl glucofuranoside and butyl glucopyranoside were the products obtained. In all tests, butyl glucopyranoside formed almost two times the amount of butyl glucofuranoside. All the catalyst showed different catalytic activities in the reaction due to the varied properties of the catalysts. While Zr-SBA-15-(1.0) as catalyst gave 3.1% yield, 1.0/SO Zr-SBA-15-(1.0) as catalyst gave 92% butyl glucoside yield in the reaction. This result indicated the importance of the acidity of the catalyst. Even though low surface area and pore diameter, the catalyst with higher acidity and higher B/L ratio provided more butyl glucoside yield. This study showed that sulfated forms of Zr-SBA-15 catalyst can be used as catalyst for the glycosidation reaction of butanol. High conversion and yield can be obtained. So, zirconium incorporated silica based mesoporous materials could be a good alternative for the homogeneous catalysts.



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