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Grafting of SBA-15 by Aminopropyltriethoxysilane for In Situ Aldol Condensation of Furfural and Acetone

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Abstract. This work aims to study the activity of SBA-15 grafted with 3-aminopropyl-triethoxysilane (APTES) in an in situ aldol condensation between furfural and acetone. The SBA-15 grafted with APTES (AP-SBA-15) was prepared in toluene by a conventional method. The grafting leads to the formation of covalent bonds between surface silanol of the SBA-15 and APTES without significant changes in the structural characteristics of SBA-15. The sample with the new surface species has smaller specific surface areas and higher basicity than the parent SBA-15. Aldol condensation was performed in an in situ reactor and monitored continuously by the ATR-FTIR technique. Because of higher basicity, the AP-SBA-15 produced furfurylbutenone (FB) formation more than the parent SBA-15. Moreover, the FB formation on the AP-SBA-15 increased with the temperature.

Keywords: SBA-15, APTES, Aldol condensation, Furfural, Acetone.

1. Introduction

Furanic compounds such as furfural and 5-hydroxymethylfurfural (HMF) are promising biomass-based feedstocks for fuels or other valued chemicals [1]. Importantly, the use of these chemicals does not compete with the needs of food crops, fodder, and natural habitat. Among such furanic compounds, furfural has been used as a platform molecule in various biomass conversions. Moreover, acetone as a by-product of phenol production has been commonly used. Both furfural and acetone are not expensive and commercially available. Hence, they can be converted to value-added chemicals such as jet or diesel fuel intermediates via a conventional aldol condensation

Aldol condensation has been widely exploited to convert biomass to desired chemicals through the formation of carbon-carbon (C-C) bonds. The reaction can be operated in either gas or liquid phase in the presence of acid or base catalysts. According to many studies, the reaction has been carried out in the presence of homogeneous catalysts which are difficult to regenerate. To solve this drawback, the procedure could be carried out with heterogeneous solid catalysts.

Numerous types of solid base catalysts such as Mg-Al layered double hydroxide (LDH), magnesia-zirconia (MgO-ZrO₂), and calcium oxide-zirconia (CaO-ZrO₂) have been used in aldol condensation. However, both leaching of active species and water interaction deactivate these catalysts [3]. To avoid this drawback, the material surface could be modified by organic molecules to form covalent bonds between a desired active group and modified support.

Grafting is among many versatile approaches to generate amino-modifying species on material surfaces via covalent bonding between an organosilane and surface silanol groups. The advantages of the method are better-defined structure and hydrolytic stability of the produced materials [4]. Various organic functional groups have been used for grafting, for example, vinyl [5, 6], sulfonic acid [7, 8], carboxylic acid [9, 10], and amines [11]. Among these precursors, 3-aminopropyltriethoxysilane (APTES) is frequently used as an organosilane due to its less steric hindrance. Moreover, the framework of porous supports can be preserved.

Mesoporous siliceous materials have been used as a support for grafting [12], for example, Tech molecular sieves (TMS), hexagonal mesoporous silica (HMS), Mobil composition of matter (MCM), Santa Barbara amorphous (SBA). Particularly, SBA-15 [11, 13] is among promising materials because of a thick pore wall [14, 15]. It has better hydrothermal thermal stability than other silica materials.

Up to date, there are no reports about the in situ catalytic studies of SB APTES for aldol condensation between furfural and acetone. This work investigates the feasibility of upgrading furfural via aldol condensation over APTES-modified mesoporous SBA-15 in an aqueous condition.

2. Experimental

2.1 Preparation of SBA-15 as a siliceous mesoporous support

SBA-15 was prepared according to the literature [11]. Pluronic® P123 (average Mw ~5,800, Sigma-Aldrich), 7.48 g, was dissolved in 305 mL of 1.5 M HCl in a 500 mL round bottom flask connected with a glass condenser. The template solution was stirred at 40 °C for 24 h. Tetraethyl orthosilicate (TEOS, 98.0%, Fluka Chemika), 17.4 mL, was slowly dropped into the template solution. The colloidal mixture was stirred further at 40°C for 5 h. Then, the mixture was twice divided into two of 270 mL Teflon-lined autoclaves. They were aged without stirring at 100°C for 24 h. The solid products were washed by deionized water until the pH became 5.5, and dried at 60°C for 12 h. Finally, the samples were calcined at 550°C for 16 h with a heating rate of 1°C/min.

2.2 Conventional grafting of SBA-15 with 50 wt. % of APTES

SBA-15 was grafted by APTES using a method from the literature [11]. SB was pre-dried at 120°C for 2 h. Then, the dried powder, 1.00 g, was suspended to 100 mL of toluene (99.5%, QRēC™) in a 100 mL round bottom flask, equipped with a glass condenser under N₂ gas flow. APTES (99%, Acrōs Organics) of 50 wt. %, 0.54 mL was added dropwise via a 1 mL plastic syringe with a needle under N₂ gas flow. The suspension was stirred at room temperature for 24 h, filtered through a thimble, washed by absolute ethanol (99.9%, Carlo Erba), extracted via a Soxhlet extractor using absolute ethanol for 12 h, and dried at 80°C for 12 h. This sample was named AP-SBA-15.

2.3 Materials characterization of SBA-15 grafted by APTES

X-ray diffraction (XRD) patterns were obtained using a Bruker XRD-D8 Advance with Cu-K_α(1.54 Å) radiation at a voltage of 40 kV and a current of 40 mA using a LYNXEYE detector with θ range from 0.5 to 5.0° with a step size of 0.02°. The interplanar spacing of the

plane (100), ($d_{(100)}$), and unit cell parameter (a_0) of the prepared samples were calculated from the following equations.

$$d_{(100)} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

$$A_0 = \frac{2d_{(100)}}{\sqrt{3}} \quad (2)$$

Nitrogen (N_2) adsorption-desorption isotherms were obtained at a temperature of -196° using a BELSORP-mini II. Before a measurement, samples were degassed at 120°C for 24 h. Both specific surface area and pore volume were calculated by a Brunauer-Emmett-Teller (BET) method. Pore size was computed from the adsorption branch using a Barrett-Joyner-Halenda (BJH) method.

FTIR spectra were collected by a Bruker Vertex 70+RamII FTIR spectroscopy equipped with an FT-Raman instrument manipulated in an attenuated total reflectance (ATR) mode using a range of wavenumber from 400 to $4,000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and a scan number of 6.

2.4 Catalytic testing of aldol condensation between furfural and acetone by in situ ATR-FTIR

In situ ATR-FTIR technique is used as a real-time analysis for an in situ aldol condensation of furfural and acetone. ZnSe was employed as an internal reflectance element. Before starting the reaction testing, the catalyst powder was dried under a hot air oven at 80°C for 3 h. The pre-dried catalyst of 10 mg was dispersed in ethanol, sonicated for several minutes, and deposited on the ZnSe surface. Afterward, the ZnSe plate was fixed on a cell holder. The mixture of furfural and acetone with the mole ratio of 1:10 was dissolved in the solution of water and ethanol with the volume ratio of 4:1. Then, the solution was introduced through the cell aligned in the in situ instrument at room temperature. IR spectra were recorded and defined.

3. Results and Discussions

3.1 Characterization results of AP-SBA-15

XRD patterns of all samples are shown in Figure 1(a). The SBA-15 shows three characteristic peaks at 0.83 , 1.44 , and 1.64° which correspond to the plane (100), (110), and (200), respectively, of SBA-15 [11]. The XRD pattern of AP-SBA-15 has a lower intensity than that of the parent. There is a slight change in the XRD peak to a higher degree. Both interplanar spacing and wall thickness are listed in Table 1. These implied that the APTES species did not change the SBA-15 structure. This finding is similar to the works of Yang *et al.* [11] and *et al.* [16].

N_2 adsorption-desorption isotherms of all samples are shown in Figure 1(b). Isotherms from all samples are type IV(a) according to the IUPAC classification [17]. It is characteristic adsorption of mesoporous materials including the formation of monolayer and multilayer on the mesopore walls before the pore condensation. Besides, all samples exhibit a type H1 hysteresis loop which indicates a narrow range of uniform mesopores wider than 4 nm [17]. Specific surface area, porosity, and pore-wall thickness of samples are summarized in Table 1. Both surface area and porosity of the grafted sample are smaller than that of the parent indicating the formation of new surface components on the support surface. Moreover, the presence of new grafting APTES species slightly increased the pore-wall thickness of the SBA-15 support according to the XRD peak shift. These results are in good agreement with the literature [11].

To further confirm the presence of new functional groups, IR spectra and peak assignment are illustrated in Figure 2. The parent SBA-15 shows the characteristic vibration modes

including the intense stretching ($\nu(\text{Si-O})$) of dense silica network, the in-plane stretching ($\nu_{\text{in-plane}}(\text{Si-O})$) of silanol (Si-OH) groups, and the symmetric stretching ($\nu(\text{Si-O-Si})$) of the siliceous framework [18]. The AP-SBA-15 shows several new vibrational bands consisting of the stretching ($\nu(\text{C-H})$) and bending ($\delta(\text{Si-C})$) of the hydrocarbon chain belonged to aminopropyl. The peak intensity of the silanol group decreases indicating the chemical bond formation through the condensation between the APTES and surface silanol of the support similar to the work by Pereira *et al.* [19]. Hence, these FTIR results confirmed the presence of new surface APTES species on the SBA-15 surface through a chemical bond formation. This finding is in accordance with the literature [11, 16, 19]

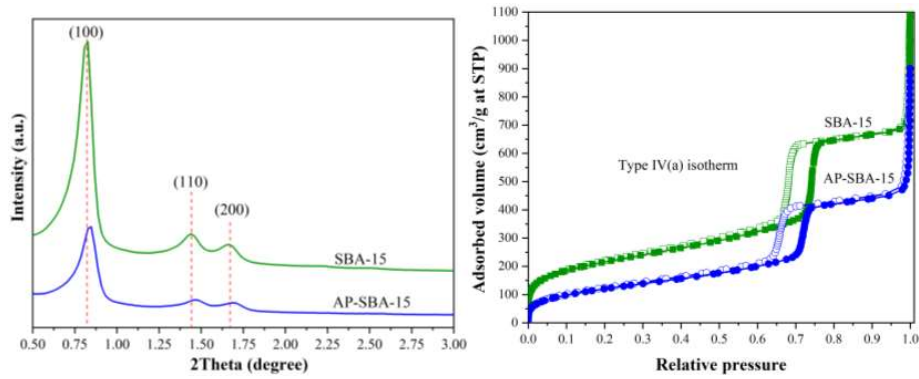


Figure 1. a) XRD patterns and b) N_2 sorption isotherms from the parent and AP-SBA15 (Filled symbol = adsorption branch and hollow symbol = desorption branch).

Table 1. Specific surface area, mesopore volume, pore diameter, and wall thickness of parent and AP-SBA-15.

| Sample | S_{BET} (m^2/g) ^a | V_{BJH} (cm^3/g) ^b | D_{BJH} (nm) ^c | $d_{(100)}$ (nm) ^d | A_0 (nm) ^e | W (nm) ^f |
|-----------|--|---|---------------------------------------|----------------------------------|-------------------------|-----------------------|
| SBA-15 | 786 | 1.00 | 8.06 | 10.67 | 12.32 | 4.26 |
| AP-SBA-15 | 434 | 0.77 | 7.06 | 10.41 | 12.02 | 4.96 |

^a S_{BET} is a specific surface area calculated by the BET method using an adsorption branch.

^b V_{BJH} is a pore volume calculated by the BJH method.

^c D_{BJH} is a pore diameter calculated by the BJH method.

^d $d_{(100)}$ is interplanar spacing at (100) plane calculated from the equation (2).

^e A_0 is a unit cell parameter calculated from the equation (1).

^f W is wall thickness calculated from $W = A_0 - D_{\text{BJH}}$.

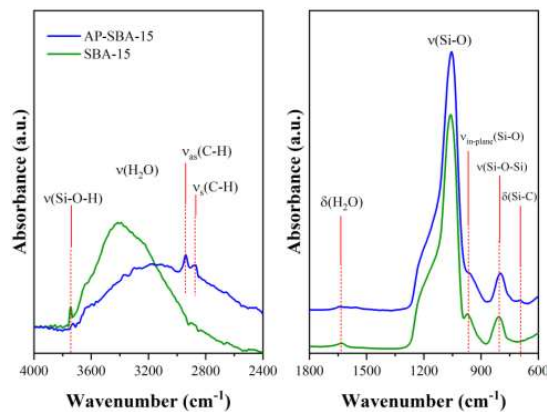


Figure 2. IR spectra and peak assignment of the parent and AP-SBA-15

3.2 In situ aldol condensation between furfural and acetone

3.2.1 Effect of surface species on catalytic activity

The aldol condensation between furfural and acetone was monitored by in situ ATR-FTIR measurements at 60°C up to 9 h. The spectra of the reaction solution under the presence of SBA-15 and AP-SBA-15 are shown in Figure 3. Two peaks at 1,284 and 1,278 cm^{-1} were assigned to the fingerprint of starting reagents and furfurylbutenone (FB) as the desired product, respectively in an aqueous solution. SBA-15 shows only the peak of the starting agents implying that it is not active because it has only weak base sites from the surface silanol group [20].

Remarkably, AP-SBA-15 provided a higher activity in terms of the FB formation sufficient base strength to generate an enolate from acetone corresponding to the work of Lauwaert *et al.* [21]. They explained that a basic amine site affected the nucleophilic addition of acetone to form an enamine intermediate before reacting with another carbonyl. These results suggested that the aldol condensation between furfural and acetone required base catalysts to facilitate the FB formation at the mild reaction temperature. Because AP-SBA-15 gave the best FB formation, it was further studied to determine the optimal temperature.

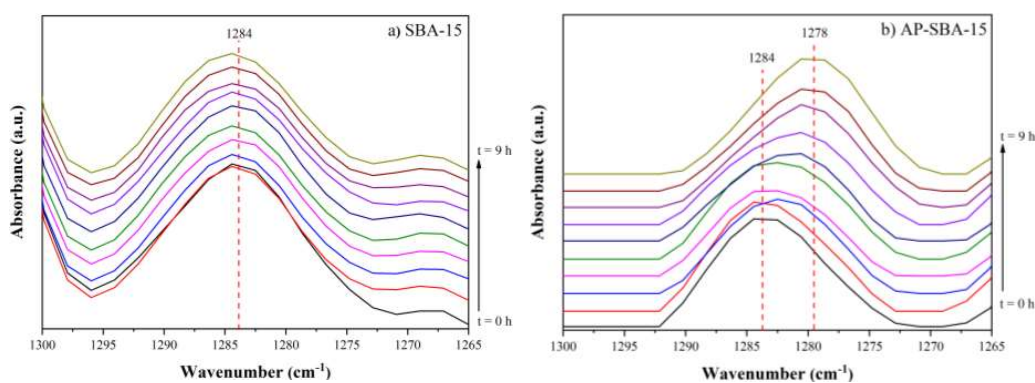


Figure 3. IR spectra of the reaction solution under the presence of SBA-15 and AP-SBA-15 during the aldol condensation between furfural and acetone at 60 °C.

3.2.2 Effect of reaction temperature on the formation of furfurylbutenone in an in situ aldol condensation

In situ IR spectra of reaction solution from the aldol condensation between furfural and acetone catalyzed by AP-SBA-15 are shown in Figure 4. The results show that the temperature of at least 40°C enables the shift of the peak at 1,284 to 1,278 cm^{-1} indicating the effect of temperature could facilitate the FB formation in the aqueous solution. Moreover, the longer reaction time gives the higher peak intensity at 1,278 cm^{-1} implying the larger FB formation was obtained. Besides, these FTIR spectra were deconvoluted to differentiate the effect of the reaction temperature in detail.

The relative peak area curves of FB at different reaction temperatures against the reaction time are shown in Figure 5. Reaction temperatures affected not only the catalytic activity but also the equilibrium of FB formation. From the curves, the FB formation increased with a reaction time until they reached 6 h. At the temperature above 50°C, the formation became nearly constant after 6 h. In contrast, at 40°C, the formation still increased. These results confirmed that the reaction depended on the temperature. This finding agrees with the literature by Heynderickx [22] studying the kinetics of aldol condensation between benzaldehyde and heptanal. It was proposed that the reaction reached equilibrium more quickly at higher temperatures.

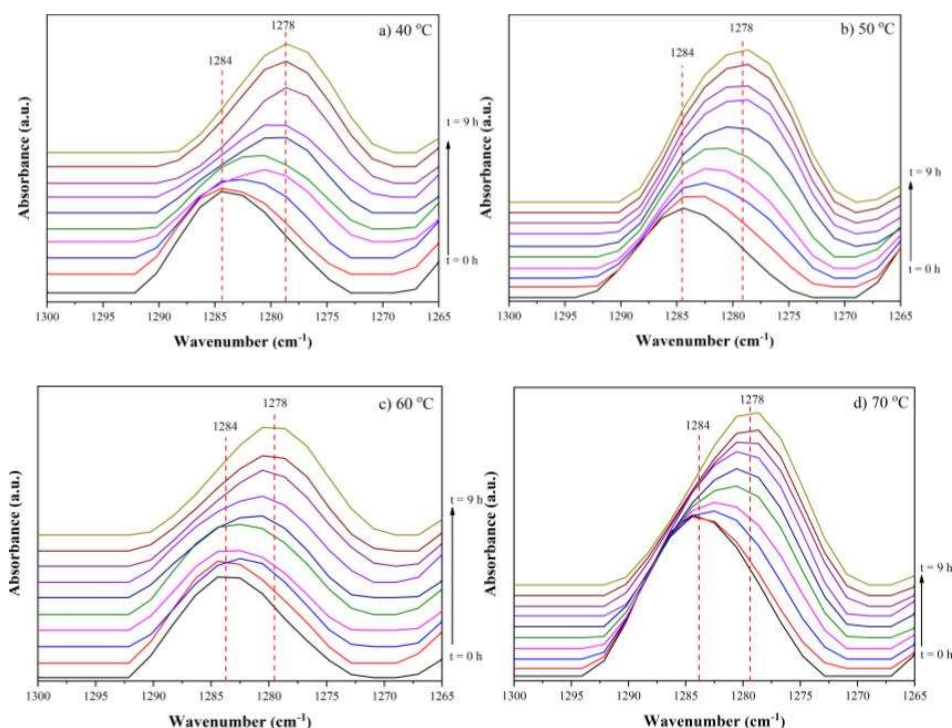


Figure 4. In situ IR spectra of reaction solution under the presence of AP-SBA-15 during the aldol condensation between furfural and acetone at various temperatures against the reaction time up to 9 h.

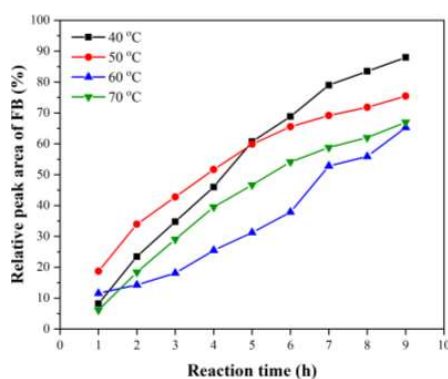


Figure 5. Relative peak area at $1,278\text{ cm}^{-1}$ of furfurylbutenone (FB) from the deconvolution results during in situ aldol condensation between furfural and acetone at various reaction temperatures

4. Conclusion

SBA-15 was successfully grafted with APTES, producing AP-SBA-15. From XRD results, the conventional grafting did not affect the characteristic structure of SBA-15. From N_2 sorption analysis, the grafting APTES species was on the pore walls of SBA-15. It was confirmed by FTIR that the grafting species chemically bonded with the silanol groups on the SBA-15 surface. The catalytic activity of the samples was evaluated in aldol condensation between furfural and acetone monitored by the in situ ATR-FTIR spectroscopy. AP-SBA-1 gave a higher degree of the formation of furfurylbutenone, while the parent SBA-15 less affected the reaction activity. The FB formation increased with the reaction time. The optimal reaction temperature for the in situ aldol condensation was 40°C . Thus, the SBA-15 grafted with APTES was proposed as a promising catalyst for the upgrading of furfural

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