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Investigation the effects of Al-grafting and calcination temperature on acidity and physicochemical properties of silica SBA-15

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Abstract: In this study, the effect of calcination temperature and Si/Al molar ratio on acidity and physicochemical properties of silica SBA-15 were investigated. Silica SBA-15 samples were calcined at 350, 450 and 550 °C, and then post-synthesis Al-grafting method was applied to incorporate aluminum species into their framework with Si/Al mole ratio of 10 and 30. Characterizations using small angle XRD and N₂ adsorption-desorption techniques indicated that hexagonal mesoporous structure was retained after performing Al-grafting even at high aluminum loading. Moreover, the FTIR results implied that aluminum species were incorporated into SBA-15 framework. NH₃-TPD results showed that by decreasing Si/Al mole ratio at all calcination temperatures, the number of weak acid sites increased in comparison to the pure SBA-15 samples. Additionally, the maximum total acidity of synthesized samples was observed at the calcination temperature of 450 °C with Si/Al mole ratio of 30.

Keywords: silica SBA-15; post-synthesis Al-grafting; acidity; physicochemical properties.

INTRODUCTION

Hydrotreating and hydrocracking processes are usually performed over bifunctional catalysts containing active metal sites for hydrogenation/dehydrogenation reactions, and acid sites for cracking hydrocarbons.¹ The catalytic performance of hydrotreating/hydrocracking catalysts can be modify by changing the nature of the active metals or the support. Hence, the modification of the physicochemical properties of the support is still one of the preferred methods used for enhancing catalytic activity.² The activity of a catalyst strongly depends on the combination of textural, chemical and physical properties of the support. Pore size is a momentous property since each catalytic system requires a unique pore size for optimal active metal loading, diffusion and selectivity. Besides, high surface area and large total pore volume usually enhance catalyst loading which increases the number of active metal sites and decreases reaction time. Moreover,

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the ability to control the acidity of the catalyst enables manufacturer to design desirable acid sites for the sake of optimizing product selectivity, activity and stability in miscellaneous catalytic applications.\textsuperscript{1-3}

In the past few years, many works have been devoted for applying mesoporous SBA-15 as a support.\textsuperscript{4-5} This material has high surface area, large pore volume and uniform hexagonal array of cylindrical mesopores. But, its lower acidity in comparison to zeolites creates a limitation for using that as a support in hydroprocessing applications. In order to increase the acidity of SBA-15, attempts have been made to incorporate heteroatom into its structure by direct or post synthesis grafting methods. However, depending on the preparation procedure, samples exhibit different structural, textural and surface characteristics.\textsuperscript{3,6} Moreover, it is reported that groups of silanol on the internal wall surface of SBA-15 are favorable for aluminum incorporation. Depending on synthesizing method and calcining temperature, the type and amount of silanol groups can be varied.\textsuperscript{6-7}

To form the SBA-15 mesostructure, a vigorous acidic reaction condition is required which is not suitable for directly incorporating aluminum into its framework. The direct synthesis of Al-SBA-15 is difficult, and is rarely stoichiometric. Additionally, it often demands fine-tuned synthesis conditions and complicated procedures.\textsuperscript{8} From this viewpoint, the development of a simple post-synthesis method for aluminating mesoporous SBA-15 becomes the last option. One of disadvantages of post-synthesis method is the formation of oxides inside the mesopores that can partially or fully block them. Therefore, surface area, total pore volume, pore diameter and order of structure, especially at high aluminum loadings are reduced. Moreover, not all of the aluminum atoms introduced are located in tetrahedral coordination in which aluminum is covalently bound to four Si atoms via oxygen bridges.\textsuperscript{8-9} Analysis performed by using $^{27}$Al MAS NMR method proves that calcining treatment after the alumination of SBA-15 samples enhances the intensity of aluminum peak in the tetrahedral coordination. Hence, more aluminum is incorporated into the SBA-15 framework.\textsuperscript{10}

Luan et al. investigated the effect of using different aluminum sources including aluminum chloride and isopropoxide, and sodium aluminate during post-synthesis of SBA-15. Results confirmed that alumination by using an aqueous sodium aluminate was the most suitable method. The $^{27}$Al MAS NMR spectra of Al-SBA-15 which was synthesized by reacting SBA-15 with sodium aluminate solution at Si/Al ratio of 20 showed only aluminum with tetrahedral coordination. Thus, aluminum was incorporated into the siliceous framework of SBA-15 due to presence of Na$^+$ ions that balance the negative charges associated with tetrahedral aluminum framework.\textsuperscript{10} This result was in line with a research was previously done by Gao et al.\textsuperscript{9}
The current research seeks to investigate the simultaneous effects of Al-grafting and calcination temperature on the acidity of SBA-15. Consideration is given to (i) the effect of calcination temperature (i.e. 350, 450 and 550 °C) and (ii) the effect of Si/Al mole ratio on specifications of Al-SBA-15 samples (i.e. 10 and 30).

**EXPERIMENTAL**

**Samples preparation**

Mesoporous SBA-15 with hexagonal \( P_{6_{3}} \text{mm} \) structure was prepared according to a well-known procedure.\(^{11-12} \) In this method, tri-block copolymer Pluronic P123 (\( M_{\text{av}}=5800, \text{EO}_{20} \text{PO}_{70} \text{EO}_{20} \), Sigma Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich, 98 %) were used as a structure-directing agent and silica source, respectively. 2.4 g of Pluronic P123 and 0.027 g of ammonium fluoride (\( \text{NH}_4 \text{F} \)) were dissolved in 84 ml of HCl (1.3 M) using a magnetic stirrer at the room temperature. Then, 5.17 g of TEOS was slowly added into the solution under vigorous stirring condition. The mixture was stirred at 18 °C for 20 h, and then aged at 130 °C for 48 h without stirring. After filtering the mixture, the remained solid was dried at 70 °C for 12 h. Finally, the calcination process was carried out in static air at 350, 450 and 550 °C for 5 h.

To obtain Al-grafted SBA-15 with a Si/Al molar ratio of 10 and 30 (theoretical content), the mesoporous silica SBA-15 used as a precursor. Additionally, sodium aluminate (\( \text{NaAlO}_2 \), Sigma Aldrich) was used for post-synthetic alumination. In grafting procedure, 0.5 g of calcined pure SBA-15 was stirred in 50 ml deionized water containing appropriate amount of NaAlO\(_2\) for 6 h. To eliminate the excess NaAlO\(_2\), the filtered materials were washed with deionized water. After drying at the room temperature for 2 days, SBA-15 products were calcined in static air at the same calcination temperature (350, 450 and 550 °C) for 5 h. According to calcination temperature (350, 450 and 550 °C) and Si/Al nominal mole ratio (10 and 30), the prepared samples were labeled as SBA-x-(y).

**Characterization techniques**

Al-grafted samples were characterized using different techniques to study their physical properties and acidities. Small-angle XRD patterns (SAXS) were recorded on an X'Pert Pro MDP using monochromatic Cu radiation with a wavelength of 1.54 Å in the low angle region (0.6° to 5.0° in the \( 2\theta \) scale). XRD patterns were recorded in the range of \( 3^\circ \leq 2\theta \leq 90^\circ \) by a Philips PW1720 diffractometer using CuK\( \alpha \) radiation (\( \lambda=1.5406 \) Å). The textural properties of samples were characterized using Belsorb Max instrument. To do such a task, 30-40 mg of a sample was degassed in preparing station under helium stream at 300 °C for 2 h, and then the device was switched to the analysis station for performing adsorption and desorption under liquid nitrogen at \(-196 \) °C. The surface area was calculated with the multipoint Brunauer-Emmett-Teller (BET) equation with linear region in the \( P/P_0 \) range of 0.05 to 0.2. The total pore volume was calculated from the maximum amount of nitrogen adsorbed at \( P/P_0 \) of 0.99. The Barret-Joyner-Halenda (BJH) method was used to determine pore size distribution. The micropore area was estimated using the correlation of t-Harkins & Jura (t-plot method). Moreover, acidic properties of the prepared samples were determined by AutoChem 2900 (Micromeritics) automatic analyzer which was equipped with a TC detector. Before \( \text{NH}_3 \) adsorption, the samples were pretreated in situ at 500 °C for 90 min under helium flow in order to remove water and other contaminants. The samples were then cooled to 150 °C and contacted with \( \text{NH}_3 \). The desorption step was performed in a helium stream (50 ml min\(^{-1}\)) with a heating rate of 10 °C min\(^{-1}\) up to 750 °C. A Fourier-transform infrared (FTIR) spectrum was
obtained using an infrared spectrometer type Bruker Vertex 70. KBr pellet technique was applied to collect infrared spectra of samples at the room temperature. Results were reported between 400 and 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

RESULTS AND DISCUSSION

In Fig. 1, the SAXS patterns of SBA-450-y samples are presented, as examples, to analyze the effect of Al-loading on the structure of samples. As seen, SBA-450-(y) samples display three well-resolved diffraction peaks, indexed as (100), (110) and (200) reflections. These samples possess highly ordered hexagonal ($P6_{3}mm$) symmetry and well-ordered mesoporous structure. Compared to the pure SBA-450, the SAXS patterns of the SBA-450-10Al and SBA-450-30Al are modified with aluminum grafting, revealing a slight structural modification of the pure SBA-450 after Al-grafting. In diffraction patterns of SBA-450-(y) samples, reflections of SBA-450-10Al and SBA-450-30Al have higher intensity compared to the pure one. Therefore, the degree of crystallinity is enhanced by grafting aluminum. Despite the higher content of aluminum, SBA-450-10Al sample has lower crystallinity than SBA-450-30Al one. This phenomenon is probably due to the formation of aluminum-oxide islands in SBA-450-10Al sample, and consequently causes a decrease in the order of structure. As a significant observation, the SAXS analysis confirms that corresponding values for all three reflections (100, 110 and 200) shift to the lower 2$\theta$ values for SBA-450-10Al and SBA-450-30Al samples. Shifting these peaks to the lower 2$\theta$ values can indicate tetrahedral coordination of aluminum in the silica SBA-15 framework which is also concluded by Mouli et al. and Luan et al. by using \(^{27}\text{Al}\) MAS NMR.\(^{10,13}\) According to those studies, shifting of 2$\theta$ in SAXS diffraction patterns to lower values may be linked with longer Al–O bond than that of Si–O. Moreover, as seen from Fig. 1, positions of peaks in SBA-450-10Al and SBA-450-30-Al samples are not significantly different. This observation indicates that these samples probably have the same size of unit cell.

![Fig. 1. SAXS patterns of the SBA-450-(y) synthesized samples](image-url)
XRD pattern of the SBA-450-10Al sample is presented in Fig. 2. As seen, the diffraction pattern of the SBA-450-10Al sample does not reveal the presence of any other crystalline phase which is probably due to the high dispersion state of the metal oxide and/or its incorporation in SBA-15 framework. It is supposed that a broad signal observed in this pattern between 2θ =15-35 ° corresponds to the amorphous silica.

![Fig. 2. Powder XRD pattern of the SBA-450-10Al sample](image)

Fig. 3 shows the N\textsubscript{2} adsorption–desorption isotherm of synthesized samples, and also their pore size distribution curves. The N\textsubscript{2} adsorption–desorption isotherm of SBA-x-(y) samples shows the typical type IV curves with a type H1 hysteresis loop at a relative pressure around \(P/P_{0}=0.7–0.8\) which is a stunning specification of well-ordered mesoporous materials. These curves represent that SBA-450-(y) and SBA-550-(y) samples have a narrow mono-modal pore size distribution centered on 10-11 nm. Conversely, pore size distribution of SBA-350-(y) samples is broader than those of other calcined samples.

Fig. 3 demonstrates that the height of hysteresis decreases by increasing aluminum content which justifies the reduction in the amount of adsorbed gases after loading the aluminum. The cutback in the height of hysteresis loop is more discernible for SBA-x-10Al samples. Furthermore, after Al-grafting, a significant variation in the hysteresis loop is not perceptible verifying the preservation of pores arrangement for those samples. Besides, N\textsubscript{2} adsorption–desorption isotherm of SBA-x-(y) samples exhibits the reduction in the capillary condensation step of Al-containing samples probably due to filling their pores by Al-oxide species.

The values of key physical parameters of synthesized samples are listed in Table 1. As seen, based on our previous study\textsuperscript{14}, by adding inorganic NH\textsubscript{4}F salt and applying low aging temperature, the mean pore diameter of samples increases in comparison to the sample synthesized using Zhao et al. method\textsuperscript{11,12}

Moreover, Table 1 shows that the BET surface areas and total pore volumes of SBA-x-(y) samples decrease due to the probability of forming Al\textsubscript{2}O\textsubscript{3} islands.
and blocking some pores after incorporating aluminum into the pure SBA-x samples. For samples calcined at 550 °C, the reduction in the surface area is more pronounced; however, this abatement (about 20% at Si/Al mole ratio of 10) is less than the value reported by Luan et al. (about 42% reduction in surface area after loading aluminum at Si/Al mole ratio of 20). Gurinov et al. concluded that significant reduction in the surface area and total pore volume of Al-grafted samples was due to a gradual filling of the rough mesoporous walls instead of forming a homogenous aluminum film. The BJH pore diameters of SBA-x-(y) samples exhibited a different trend at the same Si/Al mole ratio and did not substantially vary after Al-grafting.

Fig. 3. N₂ adsorption-desorption isotherms of a) SBA-350-(y), b) SBA-450-(y) and c) SBA-550-(y) and pore size distribution of d) SBA-350-(y), e) SBA-450-(y) and f) SBA-550-(y) samples [The curves corresponding to SBA-x-10Al and SBA-x-30Al adsorption-desorption...
isotherms are offset by 500 and 300 cm$^{-1}$ for clarity, respectively. Moreover, pore size distribution curves of SBA-350-10Al and SBA-350-30Al are shifted to 0.8 and 0.4, respectively.

The pure SBA-450 and SBA-550 samples have an equal specific surface area and total pore volume whereas pure SBA-350 sample has minimum surface area due to remaining some part of P123 surfactant in its framework even after calcination at 350 °C.

### TABLE 1. Textural characteristics of synthesized samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area, m$^2$g$^{-1}$</th>
<th>Micropore area, m$^2$g$^{-1}$</th>
<th>Total pore volume, cm$^3$g$^{-1}$</th>
<th>BJH adsorption average pore diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-350</td>
<td>439</td>
<td>65</td>
<td>1.20</td>
<td>11.73</td>
</tr>
<tr>
<td>SBA-350-10Al</td>
<td>385</td>
<td>33</td>
<td>1.08</td>
<td>11.30</td>
</tr>
<tr>
<td>SBA-350-30Al</td>
<td>409</td>
<td>39</td>
<td>1.17</td>
<td>11.48</td>
</tr>
<tr>
<td>SBA-450</td>
<td>478</td>
<td>27</td>
<td>1.25</td>
<td>11.08</td>
</tr>
<tr>
<td>SBA-450-10Al</td>
<td>412</td>
<td>22</td>
<td>1.08</td>
<td>10.89</td>
</tr>
<tr>
<td>SBA-450-30Al</td>
<td>443</td>
<td>29</td>
<td>1.19</td>
<td>10.76</td>
</tr>
<tr>
<td>SBA-550</td>
<td>497</td>
<td>30</td>
<td>1.25</td>
<td>11.02</td>
</tr>
<tr>
<td>SBA-550-10Al</td>
<td>401</td>
<td>26</td>
<td>1.04</td>
<td>10.59</td>
</tr>
<tr>
<td>SBA-550-30Al</td>
<td>442</td>
<td>26</td>
<td>1.17</td>
<td>10.83</td>
</tr>
</tbody>
</table>

FTIR spectrums recorded in the range of 400-4000 cm$^{-1}$ for SBA-450-(y) samples are presented in Fig. 4. These figures show four major peaks at 3200-3600, 1000-1250, 800 and 400-500 cm$^{-1}$. All samples exhibit broad band at 1000-1250 cm$^{-1}$ due to asymmetric Si–O–Si stretching modes (Q$^4$ sites). The bands around 800 and 960 cm$^{-1}$ are related to T–O (T= Si and Al) symmetric stretching mode, and their intensities decrease after incorporating aluminum into pure SBA-450 framework. Moreover, the band at 400-500 cm$^{-1}$ is assigned to the Si–O–H bending vibration. The broad band at 3200–3600 cm$^{-1}$ can be attributed to O–H stretching of Si–OH silanol groups (Q$^2$ and Q$^3$ sites) and Brønsted acid sites. Intensity of 1000-1250 and 3200–3600 cm$^{-1}$ peaks are smaller in SBA-450-10Al and SBA-450-30Al samples than those of pure SBA-450 demonstrating lower density of surface Si–O–Si and Si–OH in the former samples. These results are in line with Mouli et al. work that Q$^4$ sites decrease by Al-grafting in the SBA-15 framework.
It is well-known that the acidity of a catalyst strongly affects the catalytic reactions. To determine the acidity of sample, NH$_3$ temperature programmed desorption (NH$_3$-TPD) measurement is carried out. Ammonia is a basic molecule, and it is strongly adsorbed by the acidic sites. It is obvious that the more is the strength of acidic site, the greater is the desorption temperature. For SBA-x-(y) samples, NH$_3$-TPD characterization results are displayed in Figs. 5 and 6, and also Table 2. As shown, NH$_3$-TPD profile for all SBA-x-(y) samples has two peaks. The first peak from 102 °C to 214 °C corresponds to the weak acidity (mainly contributed by pentahedral aluminum species and surface hydroxyl group attached with Si or Al), and the second from 665 °C to 738 °C is attributed to strong acid sites (tetrahedral aluminum species and isolated silanols). By increasing aluminum content of samples for all studied calcination temperatures, the position of the peak attributed to the weak acidity is shifted to the higher value while irregular variation is observed in the strong acid peaks.

The pure SBA-x samples (see Table 2 and Fig. 5) have the fewest number of weak acid sites, intense peaks of strong acid sites are augmented in these samples. Aluminum grafting for samples calcined at 450 °C and 550 °C enhances the total number of acid sites but strong acid sites are partially diminished. Therefore, pure SBA-x samples have more number of strong acid sites than SBA-x-10Al and SBA-x-30Al ones. Intensifying weak acid sites by increasing aluminum content is attributed to the presence of Brønsted acid sites and the availability of aluminum species in pentahedral coordination.

The acidity of Al-grafted samples is varied even at high aluminum content but there is no significant variation in physical and structural properties of these samples. The main reason for this phenomenon is the facilitated diffusion of aluminum precursor to mesochannels of pure SBA-x particles during Al-grafting.
TABLE 2. Nature and amount of acid sites in prepared SBA-x-(y) samples with different calcination temperatures and Si/Al mole ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of acid sites, µmol / g NH$_3$ (Peak temperature, °C)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak</td>
<td>Strong</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>SBA-350</td>
<td>137 (134)</td>
<td>1180 (665)</td>
<td>1317</td>
<td></td>
</tr>
<tr>
<td>SBA-350-10Al</td>
<td>316 (214)</td>
<td>423 (678)</td>
<td>739</td>
<td></td>
</tr>
<tr>
<td>SBA-350-30Al</td>
<td>650 (182)</td>
<td>819 (684)</td>
<td>1469</td>
<td></td>
</tr>
<tr>
<td>SBA-450</td>
<td>62 (146)</td>
<td>720 (678)</td>
<td>782</td>
<td></td>
</tr>
<tr>
<td>SBA-450-10Al</td>
<td>827 (190)</td>
<td>523 (699)</td>
<td>1350</td>
<td></td>
</tr>
<tr>
<td>SBA-450-30Al</td>
<td>573 (178)</td>
<td>956 (672)</td>
<td>1529</td>
<td></td>
</tr>
<tr>
<td>SBA-550</td>
<td>52 (102)</td>
<td>248 (738)</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>SBA-550-10Al</td>
<td>731 (193)</td>
<td>378 (703)</td>
<td>1109</td>
<td></td>
</tr>
<tr>
<td>SBA-550-30Al</td>
<td>441 (179)</td>
<td>504 (697)</td>
<td>945</td>
<td></td>
</tr>
</tbody>
</table>

As seen in Fig. 6 and Table 2, the acidity of samples is adjusted by varying the calcination temperature and Al/Si molar ratio.

![Fig. 5. NH$_3$-TPD of prepared samples:](image_url)
a) SBA-350-y, b) SBA-450-y and c) SBA-550-y
Since aluminum in its tetrahedral and pentahedral coordination forms acidic sites, an increase in the amount of aluminum higher than Al/Si molar ratio of 0.033 establishes aluminum oxides in octahedral coordination. It is believed that this extra aluminum species does not affect acidity. Moreover, aluminum oxide islands are created by increasing aluminum; therefore, total acidity of samples is reduced due to overlapping acidic sites.

Furthermore, Fig. 6 shows that calcination at 450 °C with Al/Si molar ratio of 0.033 is recommended for catalysts requiring high number of acid sites. By increasing calcination temperature from 450 to 550 °C, the acidity of samples decreases due to the condensation of silanol group enabling the anchor of aluminum compounds.

CONCLUSIONS

In this research, effects of the calcination temperature and aluminum grafting on the acidity and physical properties of SBA-15 were investigated. Results obtained from SAXS, FTIR and NH$_3$-TPD techniques proved the incorporation of aluminum into the SBA-15 framework. Although values for all three reflections (100, 110 and 200) shifted to lower 2\(\theta\) value, the SAXS results illustrated that the structural order of SBA-x-(y) samples was maintained after grafting aluminum. The pore size distribution curves indicated that SBA-450-(y) and SBA-550-(y) samples had a narrow mono-modal pore size distribution even after grafting aluminum at high values. Furthermore, the specific surface area and
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total pore volume showed a maximum reduction of 20 and 17%, respectively at Si/Al mole ratio of 10. The NH$_3$-TPD results showed that the maximum number of acid sites was achievable at Si/Al mole ratio of 30, and loss of total acidity was observed by increasing aluminum content due to the appearance of octahedral aluminum species and formation of aluminum islands. Besides, the total acidity decreased by increasing calcination temperature. It should be mentioned that strong acid sites were dominant in pure SBA-x samples while in aluminum grafted samples the weak ones were assertive.

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