CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF SBA-15, KIT-6, APTS-SBA-15 AND APTS-KIT-6 MOLECULAR SIEVES

6.1 INTRODUCTION

Mesoporous SBA-15 and KIT-6 molecular sieves could exhibit a dual role to reduce dielectric constant by providing mesopores to entrap air and defective Si-OH groups to anchor APTS. The latter was expected to offer interfacial air voids. Hence both the molecular sieves were functionalized with APTS and used along with ODA for the synthesis of APTS-SBA-15/TPI and APTS-KIT-6/TPI nanocomposites. Their results of physicochemical characterizations are discussed in the following sections. The following reaction illustrates APTS functionalization of SBA-15 and KIT-6 (Scheme 6.1).

Scheme 6.1 APTS functionalization of SBA-15 and KIT-6
6.2 CHARACTERIZATION

6.2.1 X-Ray Diffraction Analysis

6.2.1.1 XRD patterns of calcined SBA-15 and APTS-SBA-15

The X-ray diffraction spectra of calcined SBA-15 and APTS-SBA-15 are shown in Figure 6.1. The XRD pattern of calcined SBA-15 showed its characteristic intense peak at 0.87° (2θ) due to (100). The peaks due to (110) and (200) were not clearly resolved. Similar spectrum was also reported in the literature (Naskar and Easwaramoorthy 2008).

![X-Ray diffraction spectra of calcined SBA-15 and APTS-SBA-15](image)

**Figure 6.1** X-Ray diffraction spectra of calcined SBA-15 and APTS-SBA-15

The spectrum of APTS-SBA15 showed similar feature as that of calcined SBA-15, but the intensity of (100) was slightly low due to APTS functionalization. The position of the peak was also shifted from 0.87 to 0.98° (2θ) after functionalization. It was ascribed to reduction of pore size as a result of APTS functionalization. The shoulder occurring at lower 2θ of this
peak showed that there was less number of pores unfunctionalized by APTS. Hence, APTS functionalization was established to occur within the pores in addition to external surface. It was also confirmed by the BET surface area results in Section 6.2.4.

6.2.1.2 XRD patterns of calcined KIT-6 and APTS-KIT-6

The X-Ray diffraction spectra of the calcined KIT-6 and APTS-KIT-6 are illustrated in Figure 6.2. The XRD pattern of calcined KIT-6 showed its characteristic intense peak at 0.97° (2θ) due to (211), and other peaks at 1.16° and 1.67° (2θ) due to (220) and (332) respectively.

Figure 6.2 X-Ray diffraction spectra of calcined KIT-6 and APTS-KIT-6

The intensity of the peak at 0.97° (2θ) due to (211) of the calcined KIT-6 was higher than that of the APTS-KIT-6. Similarly the intensity of peaks due to (220) and (332) of the calcined KIT-6 was slightly higher than that of APTS-KIT-6. The sharpness of the peaks proved orderly arrangement
of mesopores. In addition, the position of its characteristic peak of APTS-KIT-6 was also shifted from 0.97 to 1.14° (2θ). The other peaks were also slightly shifted to higher 2θ. It could happen, only if the APTS functionalization occurred inside the pore in addition to the external surface. It was also confirmed by the BET surface area results as discussed in Section 6.2.4.

6.2.2 Fourier-Transform Infra-Red Analysis

6.2.2.1 FT-IR spectra of as–synthesized SBA-15, calcined SBA-15 and APTS-SBA-15

The FT-IR spectra of the as-synthesized SBA-15, calcined SBA-15 and APTS-SBA-15 are shown in Figure 6.3. In the spectrum of the as-synthesized SBA-15, the intense broad peak at 3467 cm⁻¹ was due to OH stretching vibration of water and defective OH groups. Its bending vibration occurred at 1642 cm⁻¹. The asymmetric stretching vibration of the CH₂ group of locked in template occurred at 2925 cm⁻¹. The asymmetric vibration of Si-O-Si group gave an intense broad band at 1083 cm⁻¹. The corresponding symmetric vibration was seen at 800 cm⁻¹. The bending vibration of Si-O-Si was noted at 463 cm⁻¹. The peak at 962 cm⁻¹ was due to defective Si-O-H vibration. These OH groups were the anchoring sites for functionalization of APTS.

The spectrum of calcined SBA-15 displayed similar features as that of the as-synthesized SBA-15, but the CH₂ stretching mode of the template was absent in the spectrum. Hence the template might be completely degraded and desorbed during calcination. The peak at 962 cm⁻¹ was due to defective Si-O-H vibration. These were the anchoring sites for APTS functionalization.
The FT-IR spectrum of the APTS-SBA-15 showed all the characteristic vibrations of calcined SBA-15. In addition, the spectrum evidenced APTS functionalization by giving the characteristic CH$_2$ stretching vibrations of alkyl amino groups just below 3000 cm$^{-1}$. The bending vibration of CH$_2$ groups was seen as a shoulder just below 1500 cm$^{-1}$. The most important evidence for APTS functionalization was obtained by the complete absence of Si-O-H vibration close to 960 cm$^{-1}$. Hence most of the defective Si-O-H groups might be exploited for APTS functionalization. The NH$_2$
stretching vibrations of APTS at 3300 and 3400 cm\(^{-1}\) were not resolved due to broadening of OH stretching vibration of water. Additional evidence in support of APTS functionalization was obtained by the significant decrease in the intensity of the OH stretching vibration close to 3460 cm\(^{-1}\) and its bending vibration close to 1640 cm\(^{-1}\). As many of the defective Si-OH groups were used for functionalization of APTS, most of the absorbed water in them might be lost. APTS functionalization also afforded high hydrophobicity. The cumulative effect of all these factors decreased the intensity of the peak.

6.2.2.2 FT-IR spectra of as–synthesized KIT-6, calcined KIT-6 and APTS-KIT-6

The FT-IR spectra of the as-synthesized KIT-6, calcined KIT-6 and APTS-KIT-6 are shown in Figure 6.4. The FT-IR spectrum of the as-synthesized KIT-6 showed a broad band at 3467 cm\(^{-1}\) due to OH stretching vibration of water and defective OH groups. Presence of locked in template in it was evident by its CH\(_2\) stretching vibration at 2926 cm\(^{-1}\). The bending vibration of water occurred at 1642 cm\(^{-1}\). The CH\(_2\) bending vibration occurred as a shoulder just below 1500 cm\(^{-1}\). The asymmetric Si-O-Si stretching vibration gave an intense broad band at 1083 cm\(^{-1}\). The defective Si-O-H stretching vibration gave a highly resolved peak at 956 cm\(^{-1}\). The symmetric stretching and bending vibrations of Si-O-Si groups occurred at 799 and 463 cm\(^{-1}\), respectively. As the spectrum showed intense peak for Si-O-H vibration, it provides good scope for functionalizing with APTS.

The FT-IR spectrum of the calcined KIT-6 displayed similar features as that of the as-synthesized KIT-6. But the CH\(_2\) stretching and bending vibrations of the template were completely absent. The Si-O-H stretching vibration was clearly evident at 970 cm\(^{-1}\) even after calcination. Hence the calcined material could be well functionalized with APTS.
Figure 6.4 FT-IR spectra of as-synthesized KIT-6, calcined KIT-6 and APTS- KIT-6

The FT-IR spectrum of APTS-KIT-6 displayed similar features as that of as-synthesized KIT-6. The CH$_2$ vibrations of APTS gave a peak close to 2925 cm$^{-1}$. The N-H stretching vibration of APTS might occur close to 3300 cm$^{-1}$, but it was not resolved in the spectrum, but there was a shoulder close to it, in the band due to OH stretching vibration of water. The most compelling evidence for APTS functionalization was arrived by the complete
absence of Si-O-H stretching vibration close to 970 cm$^{-1}$. The peaks due to OH stretching and bending vibrations also showed decreased intensity due to APTS functionalization. Similar observation was also noted in the APTS-SBA-15, as discussed above.

6.2.3 Thermogravimetric Analysis

6.2.3.1 TGA of as–synthesized SBA-15, calcined SBA-15 and APTS-SBA-15

The result of TGA of as–synthesized SBA-15 is shown in Figure 6.5. The TGA trace of as–synthesized SBA-15 showed an initial weight loss below 100$^\circ$C due to desorption of water. The major weight loss of 28%, occurred at about 350$^\circ$C, was due to degradation and desorption of the template.

The result of TGA of calcined SBA-15 is shown in Figure 6.6. It showed a weight loss of 6.3% below 100$^\circ$C due to desorption of water and a weight loss at high temperatures was assigned to condensation of defective OH groups.

The result of TGA of APTS-SBA-15 is shown in Figure 6.7. It showed an initial weight loss of 5% below 100$^\circ$C due to physically adsorbed water. The weight loss above 300$^\circ$C was due to degradation of APTS. It occurred in two stages and the total weight loss due to APTS was found to be 5.4%.
Figure 6.5  TGA of as-synthesized SBA-15

Figure 6.6  TGA of calcined SBA-15
6.2.3.2 TGA of as-synthesized KIT-6, calcined KIT-6 and APTS-KIT-6

The result of TGA of as-synthesized KIT-6 is shown in Figure 6.8. It showed an initial weight loss below 100°C due to desorption of water. It was followed by a major weight loss at about 350°C due to degradation and desorption of template. The total weight loss was about 21%.

The result of TGA of calcined KIT-6 is shown in Figure 6.9. It showed a weight loss of 5.3% due to desorption of water.

The result of TGA of APTS-KIT-6 is shown in Figure 6.10. The TGA trace of APTS-KIT-6 showed an initial weight loss of 4.5% due to desorption of water below 100°C. It was followed by two stages of weight loss due to APTS. It started decomposing close to 300°C and formed a residue, and the latter further decomposed close to 500°C. The total weight loss due to APTS was found to be 5.6%.
Figure 6.8 TGA of as-synthesized KIT-6

Figure 6.9 TGA of calcined KIT-6
6.2.4 BET Surface Area Analysis

The textural characteristics of SBA-15, APTS-SBA-15, KIT-6 and APTS-KIT-6 are presented in Table 6.1. The surface area of SBA-15 (730 m$^2$/g) was very much higher than APTS-SBA-15 (317 m$^2$/g). It confirmed anchoring of APTS inside the pores, but anchoring of APTS outside the pores could not be ignored, as the FT-IR spectrum of APTS-SBA-15 showed absence of defective Si-O-H groups (Section 6.2.2.1, Figure 6.3). Similar results were also noted for KIT-6 and APTS-KIT-6 (Section 6.2.2.2, Figure 6.4).

Figure 6.10 TGA of APTS-KIT-6
Table 6.1  Textural properties of SBA-15, KIT-6, APTS-SBA-15 and APTS-KIT-6

<table>
<thead>
<tr>
<th>Mesoporous silica</th>
<th>Surface area(m²/g)</th>
<th>Average pore diameter(nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>730</td>
<td>3.89</td>
<td>0.86</td>
</tr>
<tr>
<td>APTS-SBA-15</td>
<td>317</td>
<td>2.28</td>
<td>0.18</td>
</tr>
<tr>
<td>KIT-6</td>
<td>894</td>
<td>4.79</td>
<td>1.00</td>
</tr>
<tr>
<td>APTS- KIT-6</td>
<td>420</td>
<td>2.67</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The pore diameter of SBA-15 was 3.89 nm whereas that of APTS-SBA-15 was 2.28 nm. Though the pore size might not be uniformly altered as a result of functionalization, the decrease in the pore diameter was attributed to use of the same Kelvin equation in calculating the pore diameter from nitrogen adsorption isotherm. In the XRD pattern (Figure 6.1), the peak due to (100) plane was shifted to lower 2θ, thus supporting reduction in pore size due to APTS functionalization. Similar results were also noted for KIT-6. The decrease in pore diameter as a result of APTS functionalization was also reported for SBA-15 by Min et al (2008).

The pore volume of SBA-15 (0.86 cm³/g) and KIT-6 (1.00 cm³/g) was also higher than their APTS-SBA-15 (0.18cm³/g) and APTS-KIT-6 (0.44 cm³/g) respectively. It also confirmed APTS functionalization within the pores in both the materials. Since the mesopores of both can strongly adsorb and hold APTS molecules within the pores, there is large probability for anchoring them inside the pores rather than on the outer surface. Since there are three ethoxy groups in each APTS, three adjacent defect Si-O-H groups are required for anchoring. The probability of providing such three adjacent
defective Si-O-H groups might be more for inner concave pore surface than the outer convex surface. Although, the density of defective Si-OH groups might be higher for inner pore surface than the external pore surface, SBA-15 with smaller pore diameter (3.89 nm) might have more density of defective Si-OH groups inside the pores than KIT-6 with large pore diameter (4.79 nm). So SBA-15 was to have more density of functionalization within the pores and KIT-6, outside the pore.

6.2.5 Scanning Electron Microscopic Analysis of SBA-15 and KIT-6

The SEM image of SBA-15 is shown in Figure 6.11a. Some of the particles showed spherical sponge like morphology, but others were of thick rock like structure. The particles were of different sizes. In addition small irregular crystallites were also seen. Such type of morphologies is important to lower dielectric constant, as they can hold lot of air voids between the particles.

The SEM image of APTS-SBA-15 is shown in Figure 6.11b. The large spherical sponges of parent SBA-15 (Figure 6.11a) were reduced to small crystallites. The decrease in size was attributed to sonication applied during functionalization. Such size reduction could admit enhanced APTS functionalization compared to the parent bulk particles.

The SEM image of KIT-6 is shown in Figure 6.11c. The crystals were of large irregular shape. The terrace of the crystals was not so smooth and the sides revealed piling of plates. The SEM image of APTS-KIT-6 is shown in Figure 6.11d. Here also breaking of large crystals into smaller ones as a result of sonication was clearly evident.
Figure 6.11  SEM images of a) SBA-15 b) APTS-SBA-15 c) KIT-6 d) APTS-KIT-6