IMPROVED CATALYSTS FOR HEAVY OIL UPGRADING BASED ON ZEOLITE Y NANOPARTICLES ENCAPSULATED STABLE NANOPOROUS HOST

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I   ABSTRACT

The objectives of this project are to synthesis nanocrystals of highly acidic zeolite Y, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates and evaluate the "zeolite Y/Nanoporous host" composites as catalysts for the upgrading of heavy petroleum feedstocks. Our results to date are summarized as follows. The synthesis of high surface ordered nanoporous silica of expanded pore diameter of 25 nm (larger than the standard size of 8.4 nm) using trimethylbenzene as a pore size expander was accomplished. The synthesis of zeolite Y nanoparticles with median pore size of approximately 50 nm (smaller than the 80 nm typically obtained with TMAOH) using combined TMABr/TMAOH as organic additives was also accomplished. The successful synthesis of zeoliteY/Nanoporous host composite materials by sequential combination of zeolite precursors and nanoporous material precursor mixtures was implied based on results from various characterization techniques such as X-Ray diffraction, infrared spectra, thermal analysis, porosimetry data. The resulting materials showed pore sizes up to 11 nm, and infrared band at 570 cm^{-1} suggesting the presence of both phases. Work in the immediate future will be focused on the following three areas: 1) Further characterization of all-silica and aluminosilicate mesoporous materials with expanded pore sizes up to 30 nm will continue; 2) Research efforts to reduce the average particle size of zeolite nanoparticles down to 35-30 nm will continue; 3) Further synthesis of polymer-SBA15 nanocomposites will be conducted by changing the amount and chemistry of the zeolitic precursors added; and 4) Investigation on the catalytic properties of the materials using probe catalytic reactions (such as cumene cracking), followed by catalytic testing for heavy oil conversion.

II   DISCLAIMER

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III   EXECUTIVE SUMMARY

The objectives of this project are to synthesis nanocrystals of highly acidic zeolite Y, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates and evaluate the "zeolite Y/Nanoporous host" composites as catalysts for the upgrading of heavy petroleum feedstocks. In comparison to conventionally-used zeolite Y catalysts of micron size particles, the nanocrystals (< 100 nm particle size) which will contain shorter path lengths, will allow faster diffusion of large hydrocarbon substrates and the catalysis products within and out of the zeolite's channels and cages (<1 nm size). This is expected to significantly reduce catalysts deactivation and prolong catalysts life. Encapsulating zeolite Y nanocrystals within nanoporous materials is anticipated to its external surfaces and pore entrances of the zeolite from being blocked by large hydrocarbon substrates, since these substrates will initially be converted to small molecules by the nanoporous host (a catalyst in its own right). The project consists of four major tasks as follows: a) synthesis of the nanoparticles of zeolite Y (of different chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; b) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter. This was conducted using poly (alkylene oxide) copolymers as template around which inorganic silicate precursors are organized. Subsequently removal of the copolymer will yield a mesoporous material, the pore sizes of which will depend on the number of poly (alkylene oxide) units; (d) Synthesis of "zeolite Y/Nanporous Host" composite materials as potential catalysts and (d) evaluation of the composites as catalysts for the upgrading of heavy petroleum feedstocks.

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IV INTRODUCTION

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such as X-Ray diffraction, infrared spectra, thermal analysis, porosimetry data. Work in the immediate future will be focused on the following three areas: 1) Further characterization of all-silica and aluminosilicate mesoporous materials with expanded pore sizes up to 30 nm will continue; 2) Research efforts to reduce the average particle size of zeolite nanoparticles down to 35-30 nm will continue; 3) Further synthesis of polymer-zeolite Y and polymer-SBA15 nanocomposites will be conducted; and 4) Investigation on the corrosion inhibition and other physicochemical/mechanical properties of the nanocomposites will be investigated.

V   RESEARCH PROGRESS

V-1   EXPERIMENTAL

V-1A   Verifying the Synthesis of All Silica Nanoporous Materials

All-silica nanoporous materials with expanded pore size were synthesized based on the method of Zhou *et*. al.[1] Typically, 4.0 g of surfactant (Pluronic 123 block copolymer as templating agent), a known mass of 1,3,5 TMB, 30 g of H_2O and 120g of 2M HCl solution were all mixed under vigorous stirring. 8.5 g of tetraethylorthosilicate (TEOS) was added to the homogenized mixture. The resulting mixture was continuously stirred for 24 h at $40^{o}C$. The white solution was finally crystallized in a sealed, high density polyethylene bottle at $100^{o}C$ for two days. The solid product was centrifuged, filtered, washed with deodorized water and dried in air at room temperature. The composition of the reaction mixture was as follows: 4.0 g P-123: x g TMB: $0.041TEOS:0.24HCl:6.67H_2O$, (where x = 0.0, 0.5, 1.5, 3.0, 4.5, 6.0 g).

V-1B   Verifying the Synthesis of SBA-15 in Sulfuric Acid.

The first approach was to verify that the all silica mesoporous SBA-15 could effectively be synthesized in the presence of sulfuric acid (H_2SO_4), rather than the widely used hydrochloric acid (HCl) as described in **IV-1A** above. This was done since we observed that zeolite Y nanocrystals (particle size < 80 nm) dissolved in the presence of HCl at pH < 2, but not in the presence of sulfuric acid. Therefore, any combination of zeolite Y and SBA-15 would have to done in H_2SO_4. The synthesis was conducted as follows; 4 gm of copolymer, P-123, was dispersed in 30 gm of H_2O and 60 gm of 2M H_2SO_4 solution while stirring, followed by the addition 9 gm of

tetraethylorthosilicate (TEOS) to the homogenized solution. The compositional ratio of the mixture was: 4g P-123:0.04TEOS:0.24H$_2$SO$_4$:6.7H$_2$O. The gel mixture (with pH 1.6) was continuously stirred for 24 hrs at 35°C, and then heated in a sealed polypropylene bottle at 100°C for one day (Sample ID.YG0304053). The solid product was centrifuged, filtered by suction, washed with deodorized water, dried in air at room temperature and calcined in air at 500°C.

IV-1C   Investigation on Zeolite Y Synthesis

These experiments were conducted to investigate the presence and nature of these zeolite Y seeds and nanocrystals at various stages of synthesis, to determine what stages will be suitable for their incorporation in SBA-15.

V-1C-1   Synthesis of Standard Zeolite Y

Standard zeolite Y of submicron size was synthesized for comparison purposes according to procedure of Ginter.[2] The zeolite was synthesized from a sodium hydroxide: sodium aluminate:sodium silicate reaction mixture. Generally, a solution (Solution A) was first prepared by dissolving 20 g of water, 4.0 g of sodium hydroxide and 2.1g sodium aluminate in a 50 ml plastic bottle. A 23 g aliquot of sodium silicate solution was added, the mixture stirred for 10 minutes and left for 1 day at room temperature. A second solution, (Solution B) was simultaneously prepared by vigorously mixing 131 g of water, 0.14g of sodium hydroxide and 13.1 g sodium aluminate in a beaker. Solutions A and B were combined under high shear mixing in high-speed blender, and left for one day at room temperature, followed by 22 h at 100ºC. The product was centrifuged, filtered, washed with deionized water, and dried at 110 ºC.

V-1C-2   Synthesis of Zeolite Y Nanoparticles

The synthesis of zeolite Y nanoparticles was based on the presence of organic additives in the reaction mixture. The following reagents were used: NaOH, aluminum isopropoxide-[(CH$_3$)$_2$CHO]$_3$Al, tetraethylorthosilicate (TEOS) – (C$_2$H$_5$O)$_4$Si, 25 Wt % tetramethylammonium hydroxide (TMAOH)- (C$_2$H$_5$)$_4$NOH, and tetramethylammonium bromide (TMABr)-(C$_2$H$_5$)$_4$NBr.

A general synthesis procedure was as follows: 12.8 g of [(CH$_3$)$_2$CHO]$_3$Al was dissolved in a solution of 52 g of 25 wt% TMAOH, 0.59 g of NaOH and 78 g of water. Varying amounts of TMABr was then added, followed by 27.7 g of TEOS. The clear solution was stirred in a polypropylene bottle for 1 day at room temperature, followed by several days at 100ºC. The solid product was recovered by high speed centrifugation at 15000 g for 40 minutes.

V-1D   Zeolite Y Precursor Preparation and its Crystallization

To prepare a typical zeolite Y precursor, 76.5 gm of water, 52.3 gm of tetramethylammonium hydroxide (TMAOH), 11.3 g of TMABr and 1.25 gm of aluminum isopropoxide were mixed, followed by the addition of 32 gm of TEOS. The mixture was stirred for 3 days at room temperature, then transferred to 100ºC in oven for 7 days. The molar ratio of the reaction mixture with seed ID: YG022305 was: 1.0Al$_2$O$_3$:4.4SiO$_2$:2.4TMAOH:1.19TMABr:0.048Na$_2$O:249H$_2$O. Aliquots of the precursor mixture were taken at different times, and the chemical composition and other synthesis conditions adjusted towards the synthesis of SBA-15 as described below.

V-1E   Synthesis of Zeolite Y/SBA-15 composites

Aliquots of the zeolite Y precursor mixture above (IV-1D) were taken after various aging times and temperature, and were modified as follows. Typically, 36 gm of aged precursor was mixed with 57 gm of TEOS and the combined mixture heated at 100ºC for 12 hrs. The Si/Al ratio in the precursor was 5:1, and after addition of TEOS, the Si/Al ratio was 50:1. An amount of 15.5 gm of the dilute heated mixture was then mixed with 4.5 gm of polymer, P-123, and 98.8 gm of 1.7M of sulfuric acid. This final mixture was stirred for 30 hr at 40ºC, then heated for 24 hr at 100ºC. The solid product was filtered, washed, dried at room temperature and calcined at 500°C. The final mixture had a molar composition ratio of 1.0SiO$_2$: 0.01Al$_2$O$_3$:0.013 P-123: H$_2$SO$_4$: 70 H$_2$O.

V-1D   Characterization

Powdered X-ray diffraction measurements were performed on a Phillips X-Pert X-Ray Diffractometer using Cu-K$_?$radiation (??= 0.15418 nm). Nitrogen adsorption isotherms and BET

surface area measurements were obtained using a Micromeritics ASAP 2020 Porosimeter. The samples were preheated at 200?C in nitrogen for 2 hr, and then evacuated before adsorption measurements. Atomic force microscopy (AFM) images were taken with a Thermomicroscopes AutoProbe CP Research Scanning Probe Microscope (SPM), a high-resolution SPM which employs ScanMaster, an optically based closed-loop position control system. It measures the sample position and corrects inherent piezo errors such as hysteresis, creep and cross coupling using a feedback loop. The 3-D surface topography was imaged with a gold-coated, V-shaped silicon nitride AFM cantilever having a spring constant of 0.5 N/m. Image sizes ranging from 2 x 2 microns to 500 x 500 nm were scanned at a rate of 500nm/s. The samples were scanned in air in non-contact AFM mode using a cantilever resonant frequency of 117.08 kHz. Dynamic Light Scattering was done on a Horiba 500 Particle Size Analyzer. Infrared spectroscopy analysis was performed with a Nicolet 750 Magna Infrared Spectrophotometer. Samples were prepared by mixing, small quantities of finely ground sample with of the KBr powder, pressing a wafer and placing the latter in IR path. The infrared spectra were measured with a computer aid (OMNIC) software and 100 scans were acquired. Thermal analysis (TGA) was performed on a SDT 2960 from TA instruments Inc. Milligram quantities of sample were placed in an aluminum pan. The sample was heated from room temperature to 800°C at a heating rate of 10°/min in flowing air.

VI   RESULTS AND DISCUSSION

VI-1   Synthesis of All Silica Nanoporous Materials

Figure 1 shows XRD of product obtained from the reaction mixture of molar composition 4.0 g P-123: 0g TMB: 0.041TEOS:0. 24HCl: $6.67H_2O$. The three peaks observed (1 major peak at 2 angle of ~1° and two smaller peaks at higher angles) are consistent with three dimensional hexagonally ordered nanoporous SBA-15.[1] However, peaks in X-Ray diffraction patterns of samples synthesized in the presence of TMB, (not shown), could not be resolved from the very large background scattering generated by the instrument at very low angles. The presence of TMB in the synthesis mixture is expected to enlarge the pore diameters and unit cell size of SBA-15, thus shifting the diffraction peaks to lower 2 angles. At angles of less than 1° significant background scattering was experienced on the XRD instrument, hence diffraction peaks, if present, could not be observed.
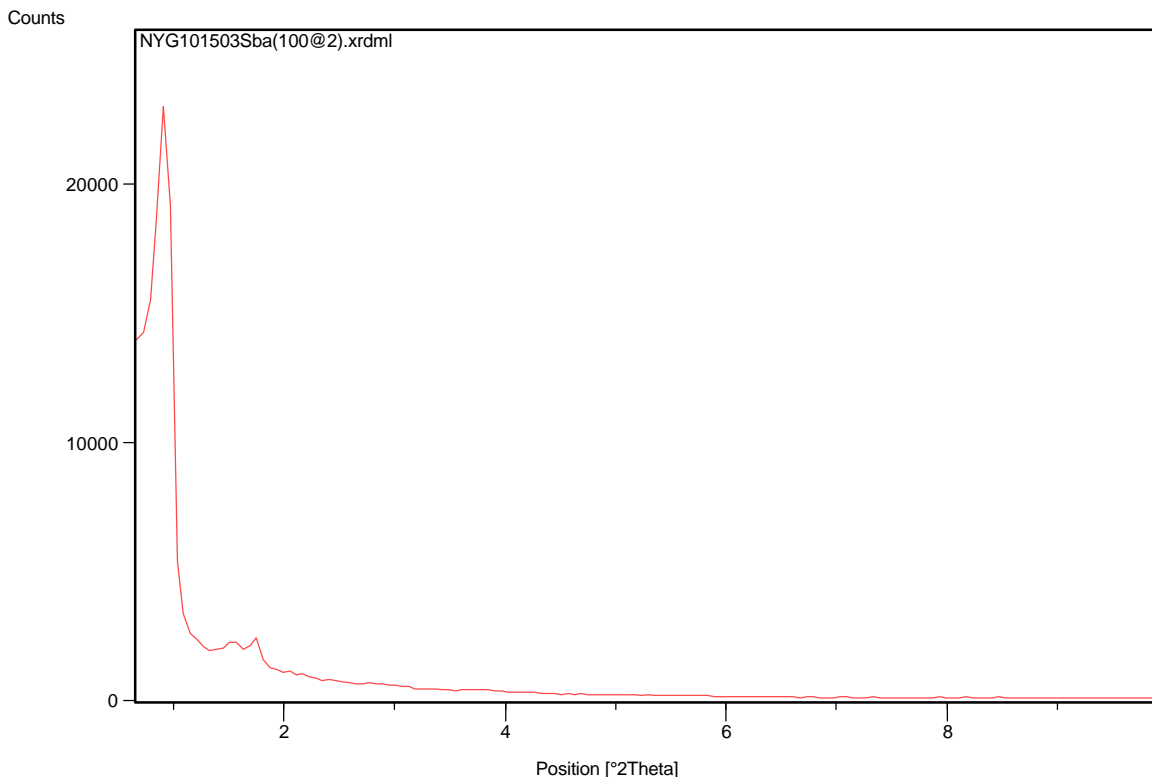
Counts

NYG101503Sba(100@2).xrdml

20000

10000

0

2   4   6   8

Position [°2Theta]

Figure 1. X-Ray Diffraction Pattern of the "as-synthesized" product obtained in the presence of HCl and surfactant P-123.

In the interim, the pore size distributions in these samples were investigated using nitrogen porosimetry. Figure 2 (top) shows the adsorption-desorption isotherms from a standard SBA-15 synthesized in the absence of TMB. A type IV isotherm was observed confirming the nanoporous (mesoporous) nature of the material, with filling of nanopores commencing at P/Po around 0.74 during the adsorption phase. A hysteresis loop, typical of this material was also observed at P/P_o values between 0.5 and 0.9. The sample shows BET surface area of 653 m^2/g, pore volume 0.67 cm^3/g and average BJH adsorption diameter of 8.4 nm.

However, SBA -15 sample synthesized in the presence of TMB (Figure 2 bottom) shows adsorption-desorption isotherms with pore filling at P/Po around 0.88 during the adsorption phase. The sample shows BET surface area of 466 m^2/g, pore volume of 1.13 cm^3/g and average BJH adsorption pore diameter of 25 nm. Pore size distribution curves for these samples are

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shown in Figure 3. Progress is therefore been made towards the synthesis of SBA-15 with expanded pore size in the range of 30 nm.
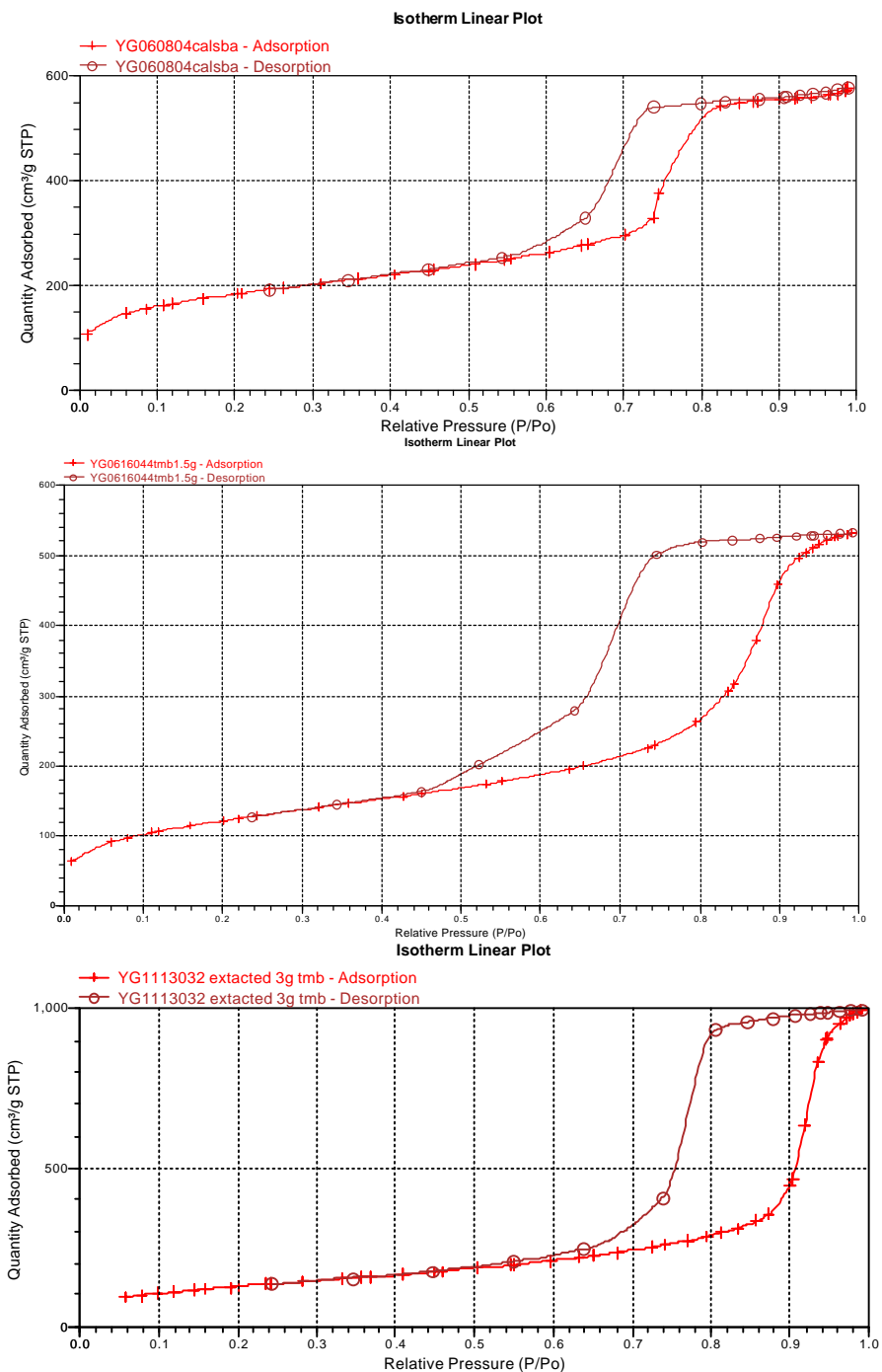

Figure 2. Adsorption-desorption isotherms of nanoporous SBA-15 synthesized in the presence of 0 g TMB (top), 1.5 g (middle) and 3 g of TMB (bottom) in synthesis mixture.
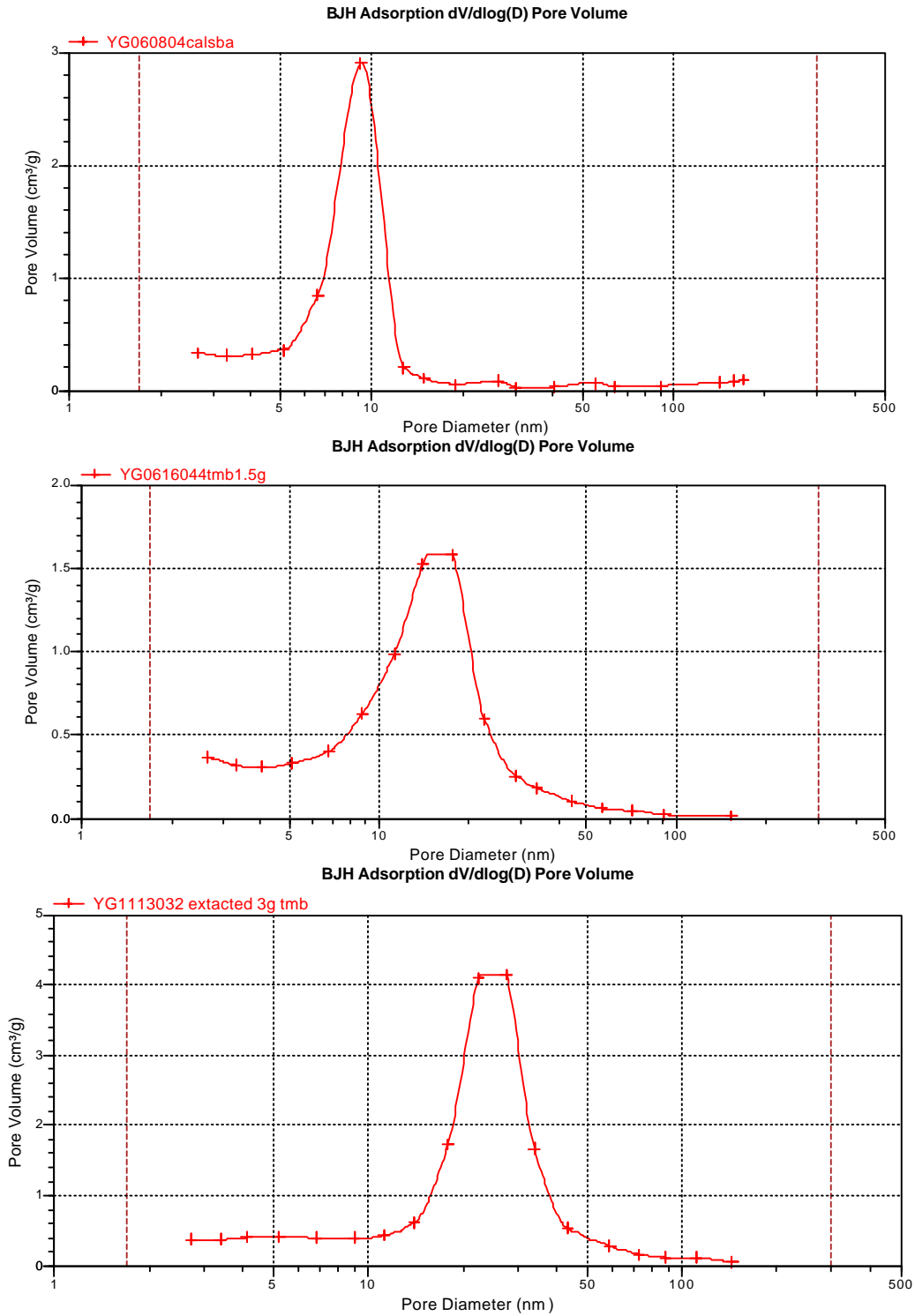
Figure 3. Pore size distribution curves of nanoporous SBA-15 synthesized with 0 g TMB (top) , 1.5g (middle) and 3 g of TMB (bottom) .

Figure 4 shows the X-ray diffraction of pure SBA-15 (A) synthesized in the presence of sulfuric acid, The XRD shows large peak around 1.0° two theta and two smaller peaks between 1.5° and 2.5° two theta assigned to the (100), (110) and (200) reflections, which are consistent with occurrence of a mesophase with well-ordered hexagonal symmetry of SBA-15. This verified that SBA-15 could be prepared in the less frequently used sulfuric acid medium, instead of the traditional and widely used hydrochloric acid medium.

Figure 4. X-ray diffraction of pure SBA-15 in the presence of H_2SO_4 (no Zeolite Y precursor added)

Figure 5. N_2 Absorption-desorption isotherms of calcined SBA-15 synthesized in H_2SO_4

BJH Adsorption dV/dD Pore Volume

Figure 6. Pore size distribution of calcined SBA-15 synthesized in the presence of H_2SO_4

Figure 6 shows the adsorption-desorption isotherms of SBA-15 synthesized in the presence of H_2SO_4. Type IV isotherms were observed, confirming that all products were mesoporous. In the case of SBA-15, inflection corresponding to filling of mesopores commenced at relative pressures (P/P_o) around 0.65 during the adsorption phase. The pore size distribution of the calcined SBA-15 (from H_2SO_4 synthesis) showed surface area of 656 m^2/g, pore volume 0.81 cm^3/g and average BJH adsorption pore diameter of 4.8 nm. These are comparable number to those obtained for SBA-15 from HCl synthesis above, except for the pore size which is approximately half.

VI-2   Comparison of Synthesis of Standard Zeolite Y and Zeolite Y Nanoparticles

Figure 7 shows the diffraction pattern of the zeolite Y synthesized (according to the method Ginter et. al[2]) for comparison purposes. The first 5 reflections at 2 angles of 7.14º, 10.1º, 12.4º, 16.1º and 20.4º are characteristic of zeolite Y.[2,3]   The low background and strong reflections indicate that the sample is highly crystalline.
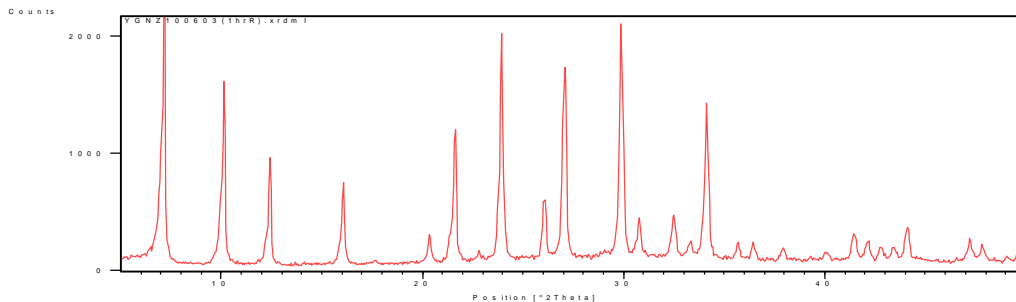
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Figure 7 XRD of standard zeolite Y synthesized in the absence of TMA cations
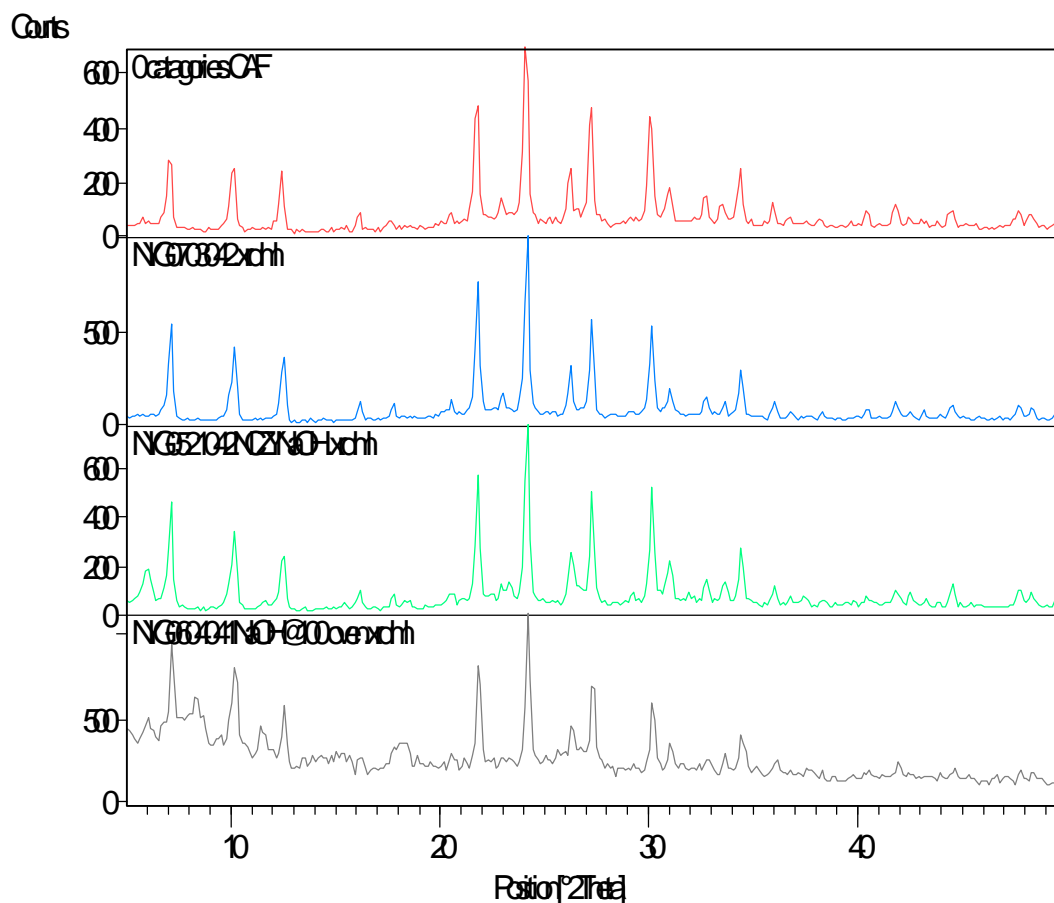

Figure 8. XRD Diffraction patterns of zeolite Y synthesized in the presence of TMAOH at 100ºC for various times (45 hrs to 168 hr from top to bottom).

Figure 8 shows XRD patterns of zeolite Y synthesized in the presence of TMAOH at 100ºC at various crystallization times (45 h to 168 h from top to bottom). No significant differences were observed between the patterns, suggesting that zeolite Y crystals are formed as early as 45 h at 100ºC in the presence of TMAOH.

In contrast to Figures 7 and 8, Figures 9 and 10 shows XRD patterns for samples obtained when TMABr was added to the TMAOH-containing mixtures. For both figures, XRD analysis shows that highly crystalline zeolite Y products were obtained in the presence of TMABr, but a sharp peak at 2 angle around 23º is predominant in all patterns. This peak became more predominant as the concentration of TMABr was increased (Figure 10) and is possibly due to the precipitation/recrystallization of the TMABr salt within the pores of the zeolite.

Figure 9. XRD patterns of zeolite Y samples synthesized in the presence of TMABr/OH (TMABr/OH ratio =0.64) with increasing synthesis time up to eight days.
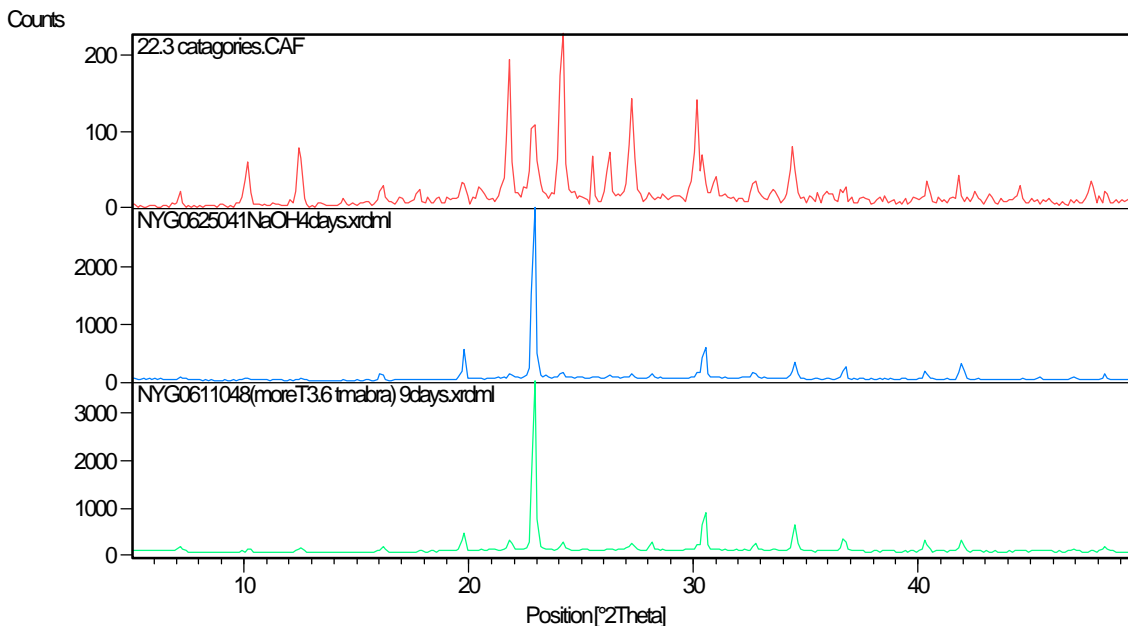

Figure 10. XRD Patterns of zeolite Y samples synthesized in the presence of TMABr/OH (TMABr/OH ratio = 1.07) with increasing synthesis time up to nine days.

The impact TMAOH and TMABr can be observed in the particle size distribution of the resulting zeolite Y products. Dynamic light scattering results (Figure 11) show that the particles size of zeolite Y synthesis under standard conditions and in the absence of organics, ranged from 100 to 1000 nm with a median of 284 nm and mean of 267 nm. However, zeolite Y synthesized in the presence of TMAOH under conditions defined above are of median sizes around 75 nm after 4 to 7 days at 100ºC (Figures 12). The morphology of these particles as obtained by AFM is show in Figure 13. At longer crystallization time (up to 196 h) particle size increased to approximately 80 nm (Figure 13).
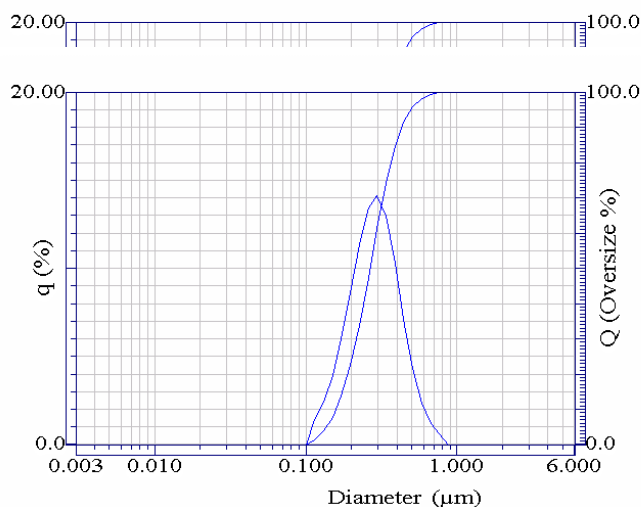

Figure 11. DLS particle size distribution of zeolite Y synthesized in the absence of TMA cation.
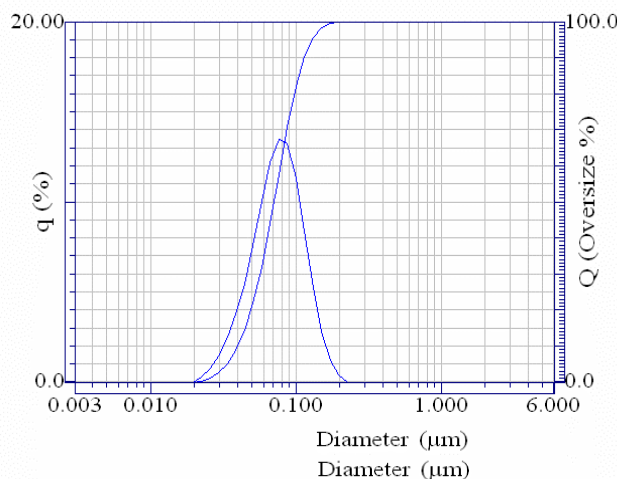

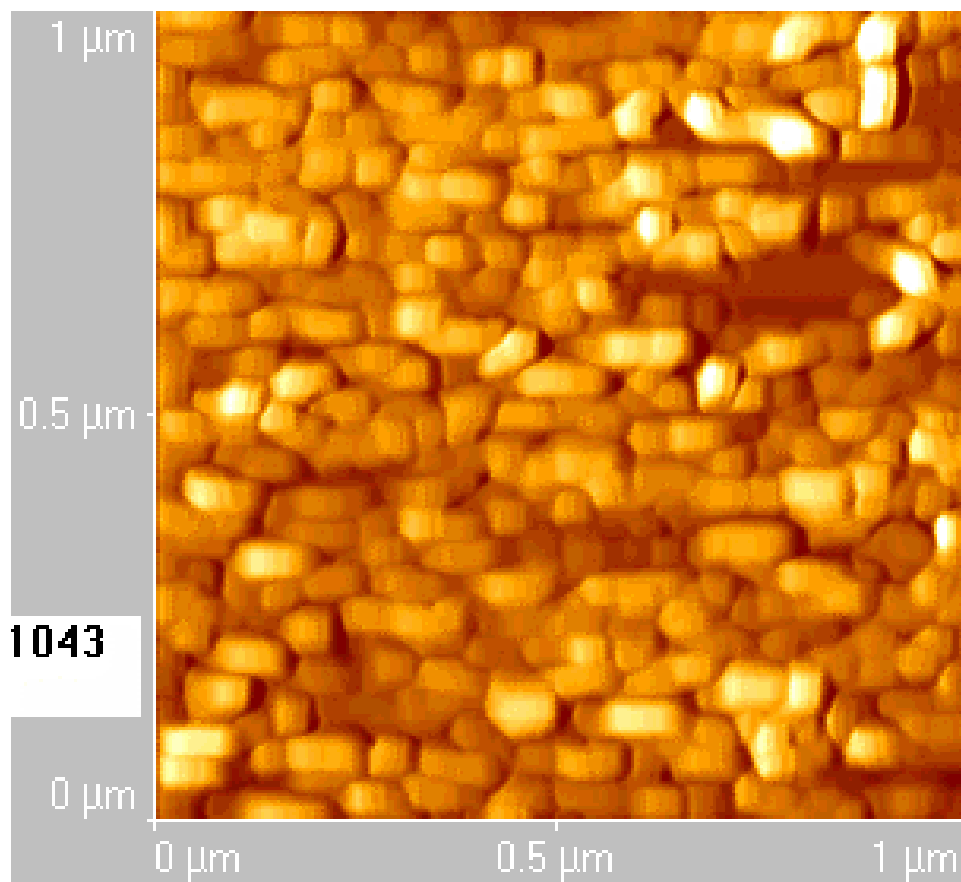**Figure 12**. DLS particle size distribution of zeolite Y synthesized in the presence of TMAOH.

Figure 13. AFM scan showing morphology of zeolite Y synthesized in the presence of TMAOH
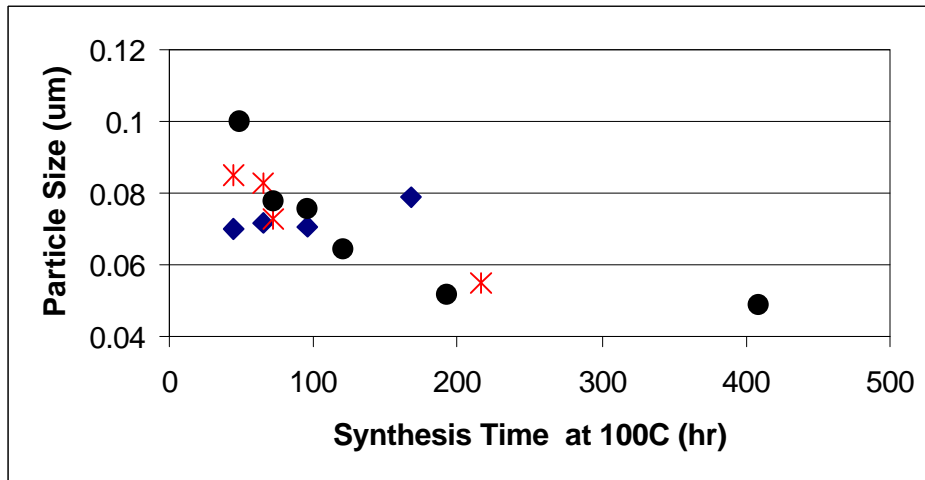
Figure 14. Median particle size of Zeolite Y nanocrystals as a function of synthesis time and with increasing concentration of TMABr (◊ - 0 TMABr, • -TMABr/ TMAOH = 0.64, ∗ -TMABr/ TMAOH = 1.07).

In the presence of TMABr however, particle size decreased with increase in synthesis time (Figure 14). After 196 h at 100ºC, the median particle size obtained in the TMABr/ TMAOH system (of mole ratio 0.64) was approximately 55 nm. Increasing the TMABr to TMABr/ TMAOH molar ratio of 1.07 showed no additional decrease in particle size of the zeolite, but XRD patterns of products obtained form the presence of additional TMABr show sharp peaks around 2 angle of 23º mentioned earlier (Figures 9 and 10) which is assumed to have resulted from the precipitation of crystalline TMABr salt. On calcination of one of these samples at 400ºC, the peak disappeared (Figure 15) possibly as a result of thermal decomposition of the salt. Higher background in the XRD of the calcined sample in comparison to its as-synthesized parent, suggests that zeolite Y looses some crystallinity during the calcinations process.
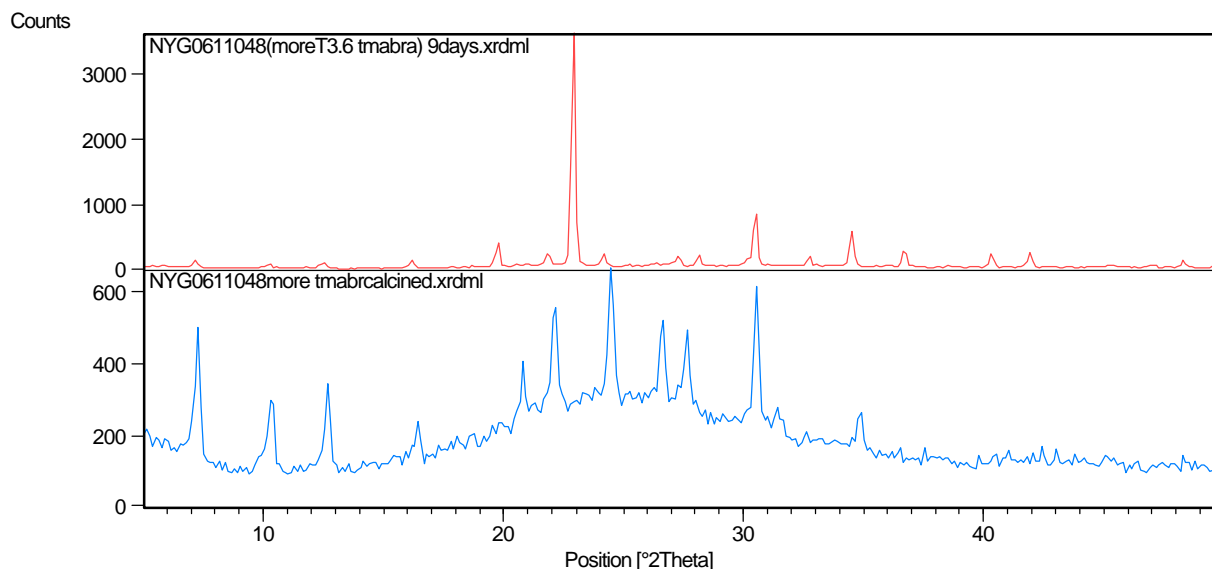
Figure 15. XRD pattern of "as-synthesized" (top) and calcined (bottom) zeolite Y nanocrystals synthesized in the presence of TMAOH/TMABr system (TMABr/ TMAOH = 1.07).

VI-3   Synthesis of Zeolite Y/SBA-15 composites

In this section we describe our research progress on the synthesis of zeolite Y/SBA-15 composites by first aging zeolite Y precursor mixtures and subsequently modified the chemical composition of the mixtures and other synthesis parameters to allow SBA-15 or related mesoporous phase to crystallize.

X-Ray Diffraction Analysis: XRDs of zeolite Y/SBA-15B composite (with zeolite Y seeds aged 100°C for 6 hrs), (Figure 16), and Zeolite Y/SBA-15B (with zeolite Y seeds aged at 100°C for 3 days), (Figure 17), each show a broad peak at two theta value around 1.5°. Smaller peaks at higher angles (1° to 2°) were not observed, possible because they were obscured by the broad peak. The broad peak and absence of the smaller peaks in each diffractogram suggest the presence of disordered mesostructured phase in each. From repeated experiments described above, we have observed (using dynamic light scattering measurements) that heated zeolite Y precursor mixtures yielded nanocrystallites of zeolite Y after aging for 6 hr at 100°C. It is possible therefore, that nanocrystals of zeolite Y could be trapped within the pores of SBA-15 mesophase (or the

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mesopores of SBA-15 could have organized themselves around the smaller crystallites of zeolite Y).
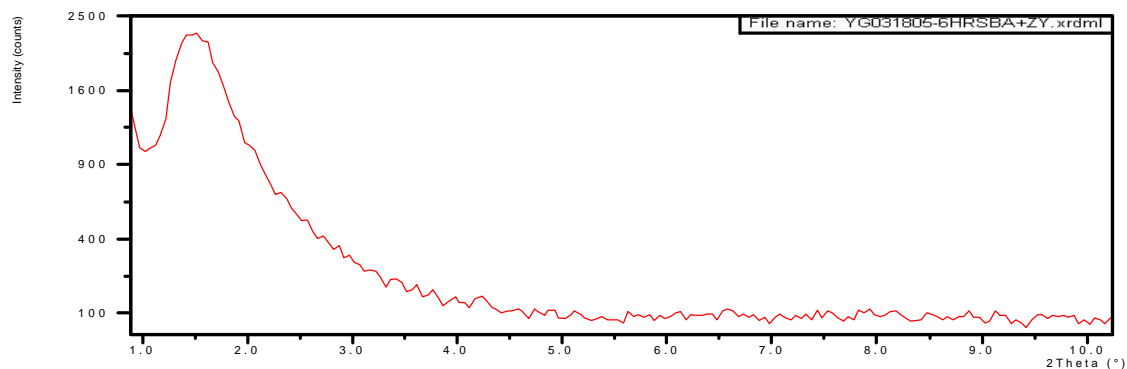

Figure 16. X-ray diffraction of zeoliteY/SBA-15B composite (with zeolite Y seeds aged at RT plus 100°C for 6 hrs)
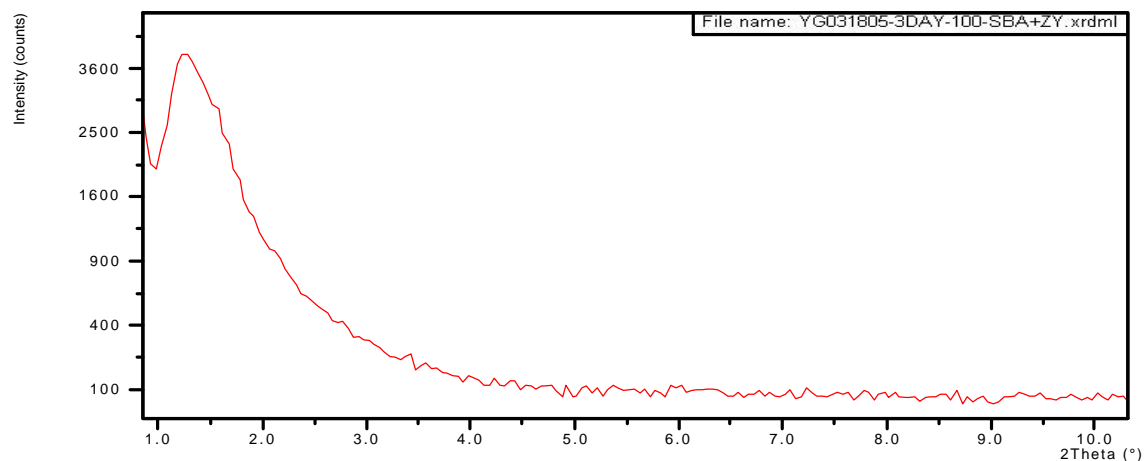

Figure 17. X-ray diffraction of zeolite Y/SBA-15C composite (with zeolite Y seeds aged at RT plus 100°C for 3 days hrs)

Porosimetry and Surface Area analysis: Figures 18 and 19 show the adsorption-desorption isotherms of (B) zeoliteY/SBA-15B composite (with zeolite Y seeds aged at RT plus 100°C for 6 hrs, and (C) zeoliteY/SBA-15B composite (with zeolite Y seeds aged at RT plus 100°C for 3 days) respectively. Type IV isotherms were observed in all, confirming that all products were mesoporous. In the case of SBA-15, inflection corresponding to filling of mesopores commenced at relative pressures (P/P$_o$) around 0.65 during the adsorption phase. In the case of the composite materials, filling of mesopores commenced at higher P/Po, 0.7 for zeoliteY/SBA-15B, and 0.8 for

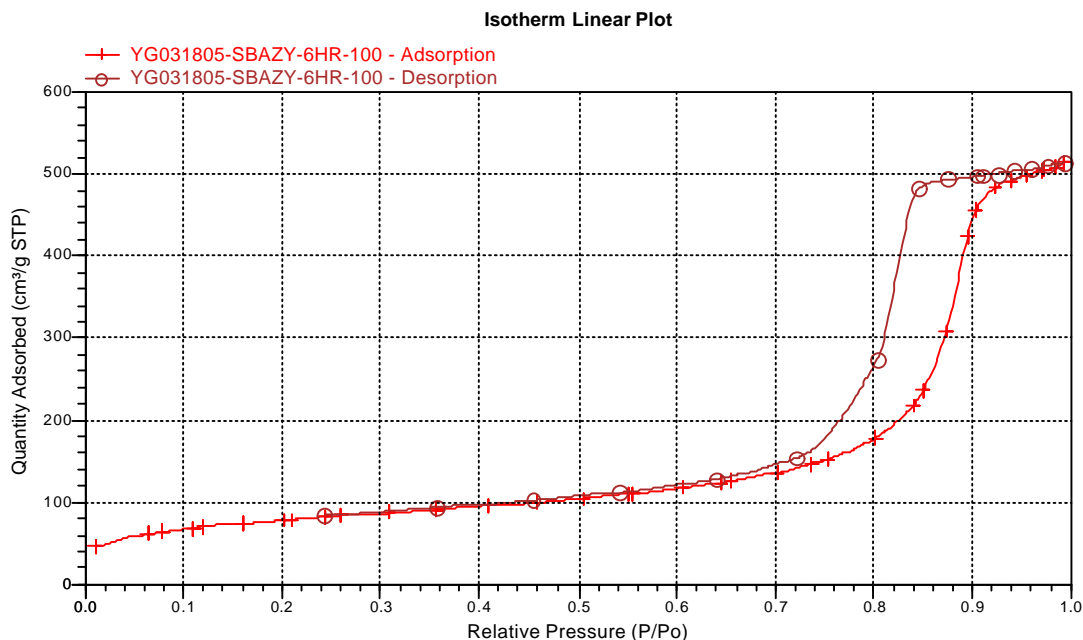zeoliteY/SBA-15C suggesting a correlation between zeolite Y precursor aging and pore size of the resulting mesophase.

Figure 18. N_2 Absorption-desorption isotherms of calcined of Y/SBA-15B composite synthesized form zeolite Y precursor aged at RT plus 100°C for 6 hrs
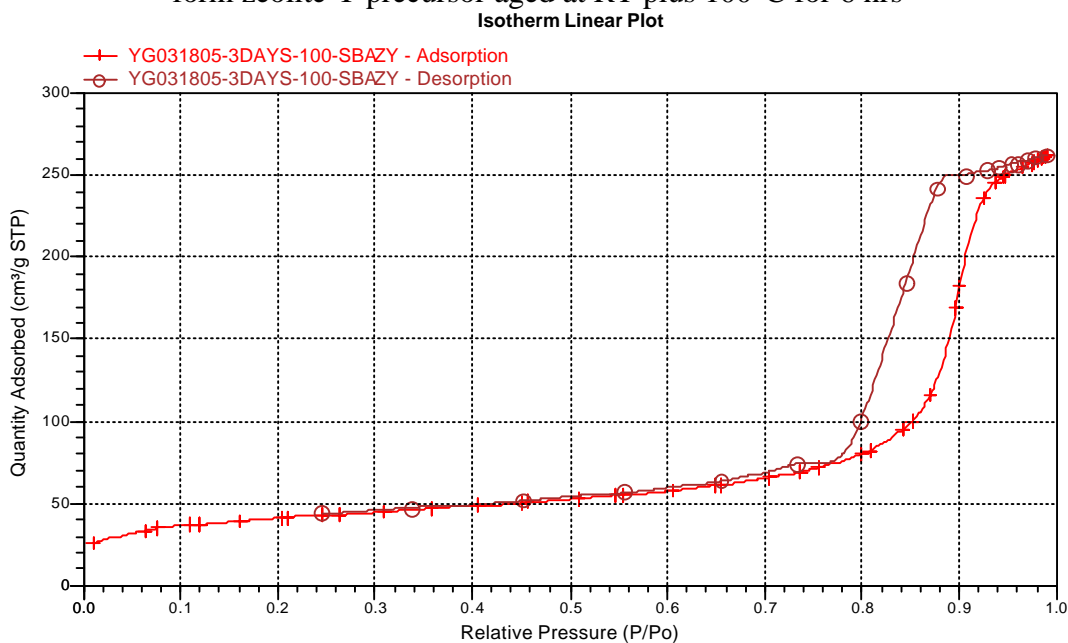

Figure 19. N_2 Absorption-desorption isotherms of calcined zeolite Y/SBA-15C nanocomposite synthesized from zeolite Y precursor aged at RT plus 3 days and at 100°C for 3dys.

BJH Adsorption dV/dlog(D) Pore Volume

Figure 20. Pore size distribution of calcined Zeolite Y/SBA-15B nanocomposite synthesized from zeolite Y precursor which was aged at room temperature for 3 days and at 100°C for 6 hr.
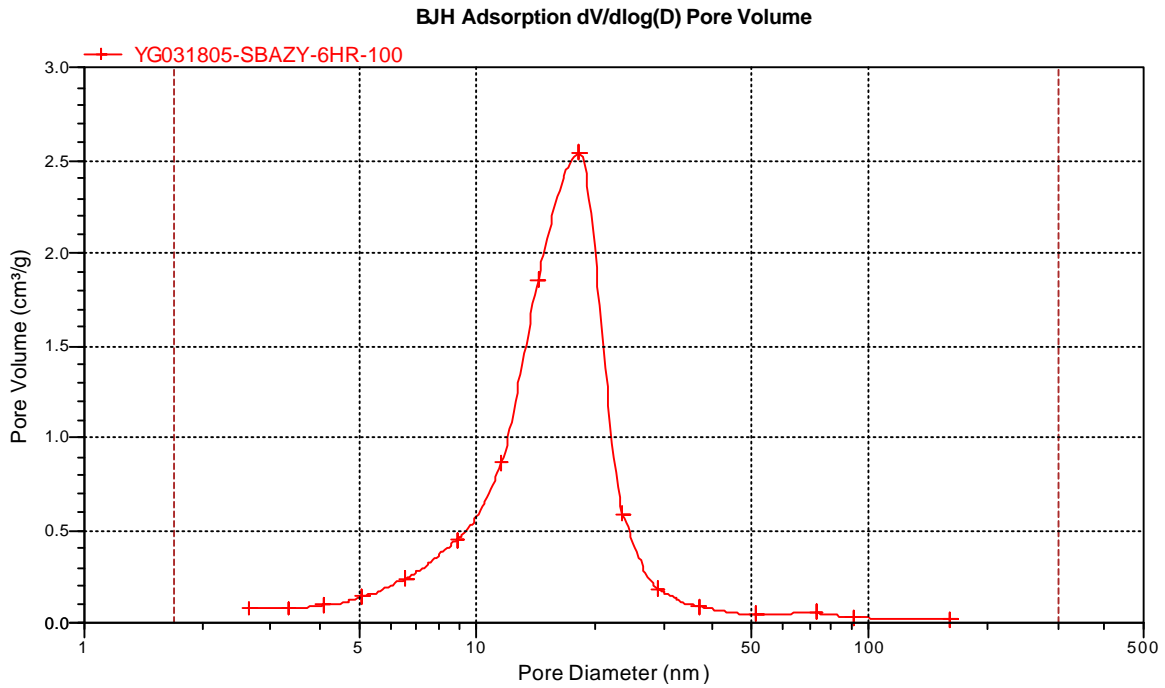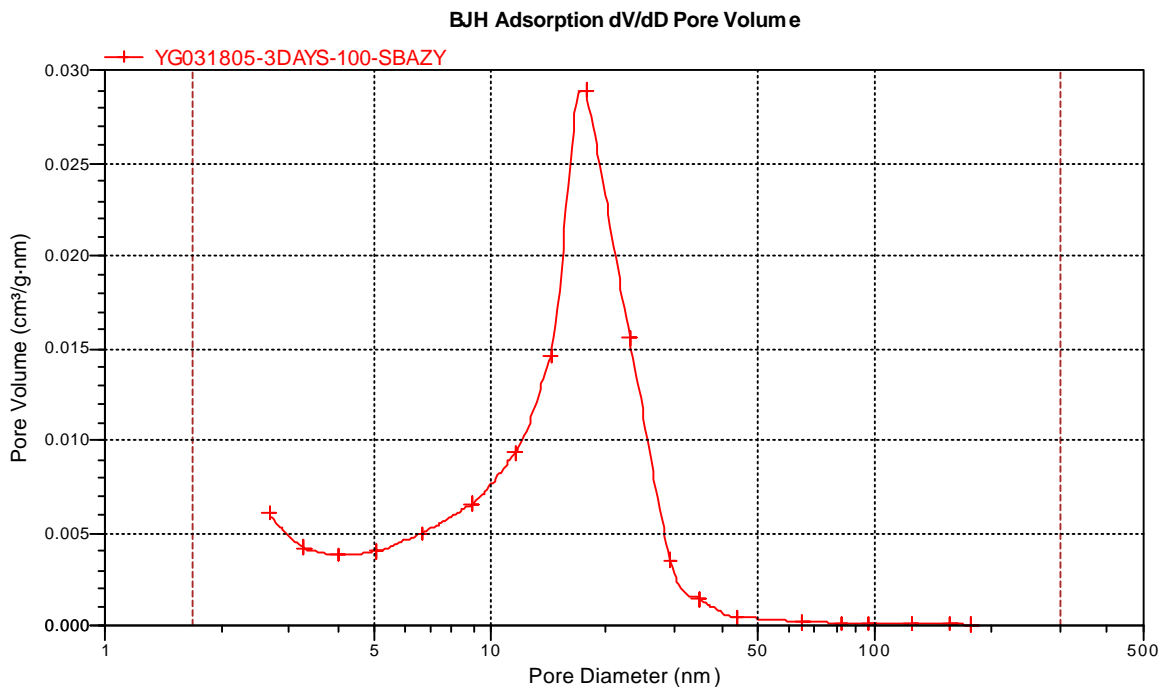
BJH Adsorption dV/dD Pore Volume

Figure 21. Pore size distribution of calcined Zeolite Y/SBA-15C nanocomposite synthesized from zeolite Y precursor which was aged at room temperature for 3 days and at 100°C for 3 days.

Table 1. Pore sizes distribution and surface areas of SBA-15 and Zeolite Y/SBA-15 composites

Sample ID	Time in days at 100°C	Surface area in m²/g	Pore size (nm)
Pure SBA-15 from H₂SO₄	2	653	4.8
Zeolite Y/SBA-15 YG031805-RT	0	158	11.3
Zeolite Y/SBA-15B YG031805-6hrs	0.25	271	11.3
Zeolite Y/SBA-15 YG031805-1day	1	239	14.1
Zeolite Y/SBA-15C YG031805-3day	3	142	11.2
Zeolite Y/SBA-15 YG031805-4days	4	242	11.7

Pore size distribution and surface area analysis of calcined zeolite Y/SBA-15B , nanocomposite synthesized from zeolite Y precursor which was aged at room temperature for 6 hr (Figure 20 and Table 1) showed surface area of 271 m²/g, BJH adsorption pore volume of 0.79 cm³/g, and pore size of 11.3 nm. Calcined zeolite Y/SBA-15C nanocomposite synthesized from zeolite Y precursor which was aged at room temperature for 3 days and at 100°C for 3 days (Figure 21 and Table 1) showed surface area of 142 m²/g, adsorption total pore volume of pores of 0.40 cm³/g, and BJH adsorption average pore width 11.1 nm.

FTIR Spectra comparing zeolite Y, SBA-15 and zeolite Y/SBA-15 composite: Figure 22 shows IR spectra of several samples. The IR spectra of pure zeolite Y (2nd from top left), zeolite Y/SBA-15B and zeolite Y/SBA-15C composites (1st and 3rd spectra from top left) all contain bands at 570 and 470 cm⁻¹. The band at 470 cm⁻¹ is assigned to the structure insensitive T-O bending modes for tetrahedral TO_4 units (T= Si or Al). The band at 570 cm⁻¹ is attributed to the double ring external linkage associated with the FAU[4] and other zeolitic structures such as MFI.[5] Both peaks are present in all samples, with varying intensities. A potentially rational conclusion is that zeolite Y is present in the material. However, the 570 cm⁻¹ peak is also observed in the pure

SBA-15 sample (4th spectra from top left), though to a much smaller extent, thus make it impossible to assign this peak exclusively to zeolite Y, and to conclusively confirm the present of the zeolite, within the SBA-15 matrix. This was similarly observed by Carr *et.* al. in their attempts to synthesize MFI-SBA-15 composite materials.[6] The 570 cm^{-1} peak in SBA-15 is not assigned, since this material contains no double six membered rings. However from a visual inspection, it can be seen that the 570/470 cm^{-1} peak height ratio is much higher for Zeolite Y/SBA-15C composite synthesized from seeds heated at 100°C for three days, compared with the ratios for pure SBA-15, zeolite-Y/SBA-15 A (with zeolite Y seeds preheated at 100°C for 6 hrs) or for Zeolite Y/SBA-15B (with zeolite Y seeds kept at room temperature for three days). Further characterization, such as acid catalyzed reactions are being conducted to further investigate the presence of zeolite Y.
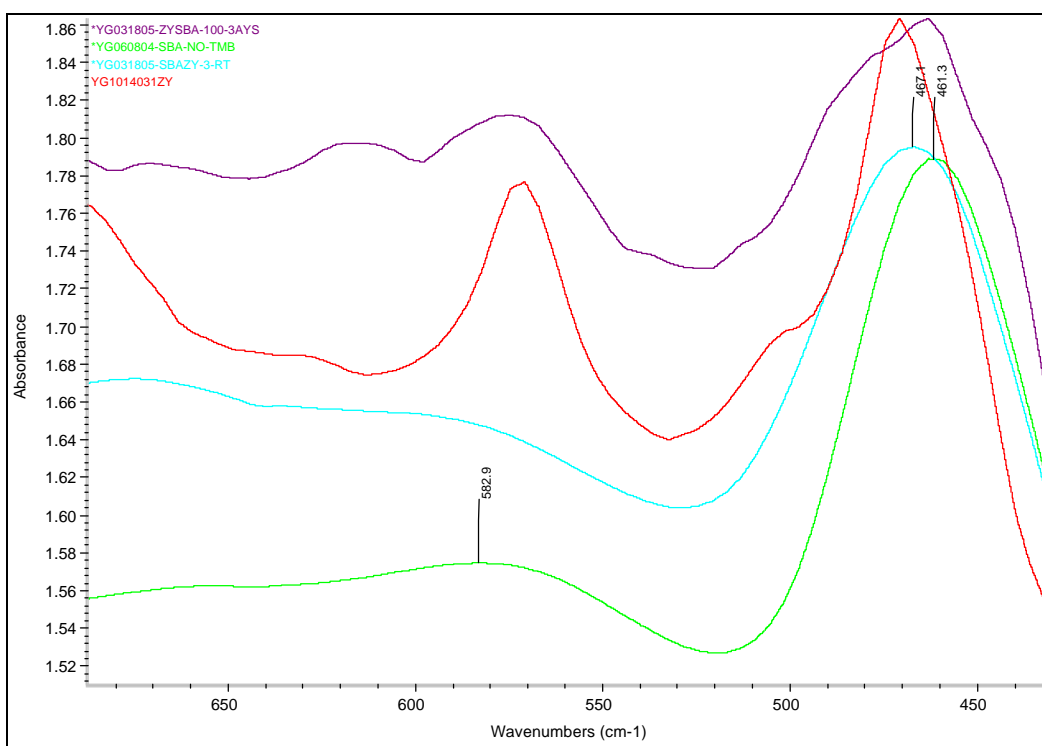

Figure 22: FTIR Spectra of (a) Pure SBA-15 synthesized in H_2SO_4 (4th from top left), (b) Zeolite Y/SBA-15B (1st from top left), (c) Zeolite Y/SBA-15C (3rd from top) and (d) Pure zeolite Y nanocrystals (2nd from top left).

Thermal Analysis: Figure 23 shows weight loss analysis curves for pure zeolite Y nanocrystals synthesized in the presence of TMAOH/Br (broken line 070304) and pure SBA-15 synthesized from H_2SO_4 (solid line 030405). Weight loss events in the zeolite Y nanocrystals in the 200 to 400°C region are attributed to the decomposition of TMAOH/Br entrapped within the pores of the zeolite. Weight loss in pure SBA-15 is attributed to the decomposition of P-123 copolymer entrapped within the mesopores. Figure 24 shows weight loss events for the zeolite SBA-15 composite. Events between 175 and 400°C suggest the presence of both SBA-15 and zeolite Y phases.
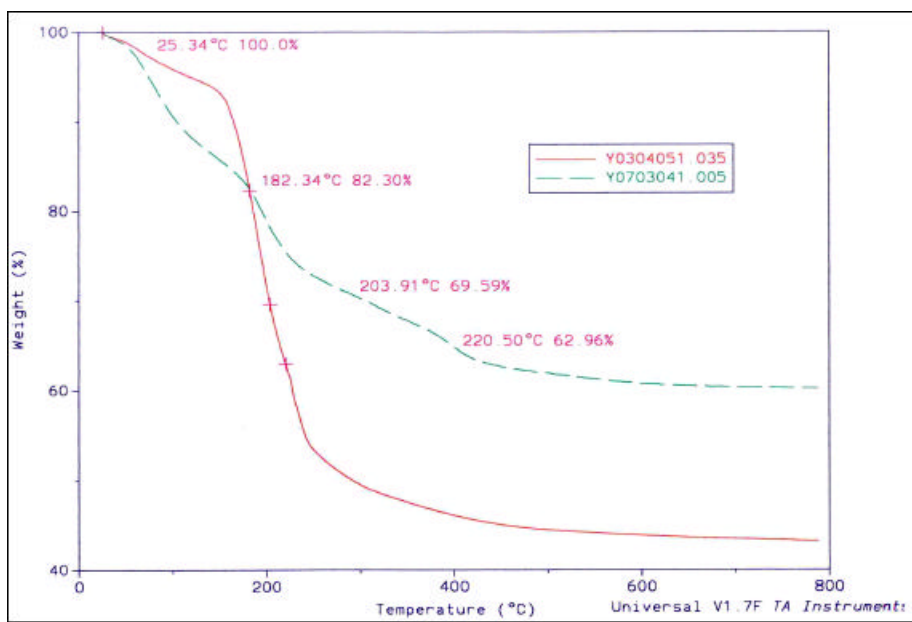

Figure 23: TGA Analysis of Pure nanocrystalline Zeolite Y (broken line with ID 070304) and Pure SBA-15 synthesized in sulfuric acid (solid line with ID 030405)
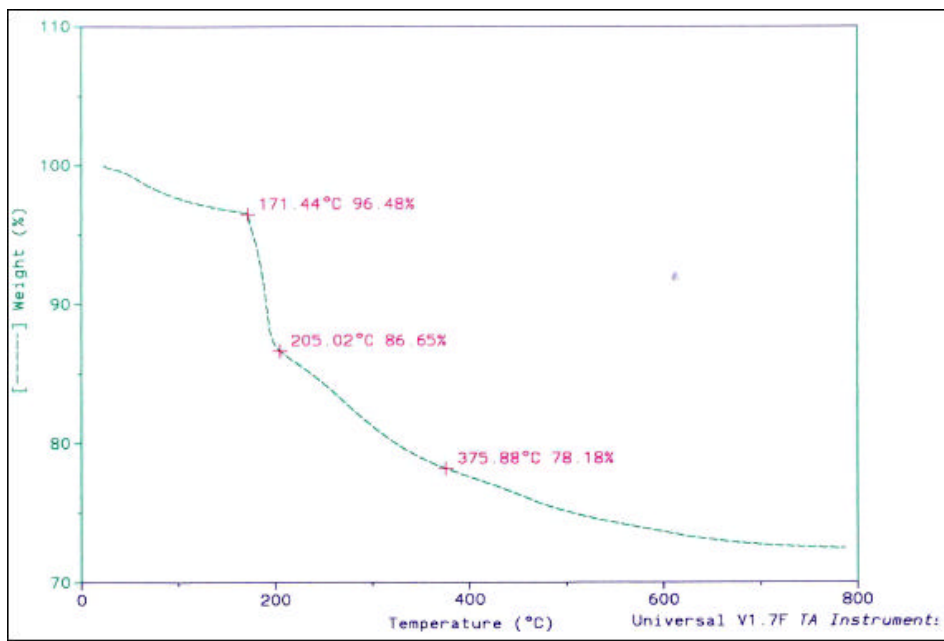
Figure 24: TGA Analysis of Zeolite Y /SBA-15 composite

VII   CONCLUSIONS

The synthesis of high surface ordered nanoporous silica of expanded pore diameter of 25 nm (larger than the standard size of 8.4 nm) using trimethylbenzene as a pore size expander was accomplished. The synthesis of zeolite Y nanoparticles with median pore size of approximately 50 nm (smaller than the 80 nm typically obtained with TMAOH) using combined TMABr/TMAOH as organic additives was also accomplished. The successful synthesis of zeoliteY/Nanoporous host composite materials by sequential combination of zeolite precursor mixtures and nanoporous material precursor mixtures was suggested from results from various characterization techniques such as X-Ray diffraction, infrared spectra, thermal analysis, porosimetry data. The composites were nanoporous of pore size larger than the pure nanoporous host. The surface area of the composite was also lower than the pure nanoporous hosts. Evidence of the presence of zeolite Y in the composite was observed in infrared spectrum.

VIII FUTURE WORK

Further characterization to understand the incorporation of zeolite Y precursor or small crystallites within the pores of SBA-15 will continue. To investigate this, we will convert all exchangeable ions to H+ by ion exchange with ammonium nitrate, followed by calcinations at 550. The presence of any acid sites using the adsorption of absorption of bases such as ammonia or pyridine. Acid catalyzed reactions will be will also be used as a means to very the existence of Bronsted acid site from the presence of zeolite Y in the material. The catalytic performance of the zeolite Y/SBA-15 composite materials will be compared with that of pure SBA-15. The catalysts will then be evaluated for the conversion of heavy petroleum feedstocks.

IX TECHNOLOGY/INFORMATION TRANSFER

Students:

Two following two students have been working on the project since inception:

Yohannes Ghirmazion   M.S. graduate student (Chemistry)
Fengling Ding   M.S. graduate student (Chemistry)
Ifedapo Adeniyi   Sophomore undergraduate (Chemistry & Engineering)
Taurean Hodges   M.S. graduate student (Chemistry)
Selassi Blavo   Senior (Chemistry and Chemical Engineering)

Presentations:

1) Synthesis of Mesoporous Solids Containing Zeolitic Phase from Hydrothermal Treatment of Colloidal Zeolite Y Precursors submitted, by Yohannes Ghirmazion and Conrad W. Ingram, to be presented in the *Materials Chemistry and Nanotechnology Symposium* at **PACIFICHEM 2005** , Honolulu, December 15-20, 2005
2)   Preparation of Nanosized micro/mesoporous composites via sequential synthesis of zeolite Y/SBA-15 phases; Yohannes Ghirmazion and Conrad W. Ingram, to be presented at the ACS National Meeting, Washington DC, August, 2005 .
3) On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide, Yohannes Ghirmazion* and Conrad W. Ingram, presentated at the 227 ACS National Meeting, Anaheim, California, March 28 - April 1, 2004 .
4) Non Ionic Surfactant Mediated Templated Synthesis of Phenylene-Bridged Organosilicate, Yohannes Ghirmazion*, Conrad Ingram, presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.

5) A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nononionic and Cationic Surfactants, Yohannes Ghirmazion*, Conrad Ingram presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.

6) Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis, Conrad Ingram* and Yohannes Ghirmazion, presented at the 4th International Mesostructured Material Symposium, May 1-4, 2004, Cape Tow, South Africa.

7) Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent was presented at the 4th International Mesostructured Material Symposium, May 1 -4, 2004, Cape Tow, South Africa.

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