



Synthesis and characterization of SiO₂-Al₂O₃ composite: Structural and surface properties

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ABSTRACT

Composites with high surface area are excellent supports used in catalysis. Silica-alumina composite (SAC) comprised of silicon and aluminium oxides were synthesized by microwave, co-precipitation and sol-gel methods. Physico-chemical properties of the composites were evaluated to determine surface area, pore volume, pore size, average particle size, total acidity and structural properties. As observed from BET surface analysis, composites have average particle size in the range of 13-19nm, surface area is 324-453 m²/g, pore volume is 0.35-0.70cc/g and total acidity is 0.314–0.392mm/g. All three methods are suitable for the synthesis of new composites of SAC type, however synthesis by microwave route could help in exponential increase in surface area and other properties.

Keywords: surface area, silica-alumina composites (SAC), microwave synthesis, total acidity

INTRODUCTION

Solid acid catalysts, such as mixed metal oxides represent an important group of materials with numerous industrial applications. Pure Al₂O₃ carriers have small specific surface area, low thermal stability and high price that make them unsuitable for industrial applications. In order to overcome these drawbacks, increasing attention has been paid to the development of composites by combining higher surface area and thermal stability of silica with the unique acidic properties of Al₂O₃. SACs are potentially useful in a number of technological applications, including catalysis. The SAC system is widely used as potential catalytic material in Diels Alder reactions [1,2], isomerization of 1-butene [3], dehydration of 2- propanol [4,5], cracking of cumene [5,6] and Friedel Craft's alkylation[7,8].The properties of silica have been extensively studied by many authors, due to its wide range of applications [9, 10]. Combination of silica with a large number of other oxides has been reported[11].Traditional mixed oxide preparation techniques, such as calcination of a mechanically ground mixture of two oxides (or oxide precursors) producing mixed oxides as a physical mixture with low surface area and porosity are unattractive for their suitability as industrial catalysts [12, 13].

Different methods, such as co-precipitation, hydrothermal, chemical vapor deposition (CVD), and colloidal and polymeric sol-gel routes have been reported for the synthesis of aluminosilicates [14-16]. Present investigation focuses on the synthesis of SAC system by co-precipitation method, sol-gel method and microwave reactor method. Structures of silica and alumina indicate the presence of Bronsted acid sites for SiO₂ and Lewis for alumina, making the composite interesting from catalytic point of view. These composites were characterized by X-ray diffraction

(PXRD), nitrogen physisorption(BET), fourier transform infrared spectroscopy (FTIR), temperature program desorption(TPD), temperature program reduction(TPR)and scanning electron microscope(SEM).The goal of the present work was to obtain mesoporous and highly acidic SAC systems in order to use them as support material for the catalyst.

EXPERIMENTAL SECTION

Freshly prepared solutions were employed for all the synthesis work. Tetraethoxyorthosilicate (TEOS) used was supplied from Sigma-Aldrich, while $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and HNO_3 were from Fisher scientific. Ammonium hydroxide from SDFine and ethanol was from China chemicals. Double distilled water was used for washings. All the chemicals were of AR grade.

1.1 Synthesis of Mixed Oxides

1.1.1 Co-Precipitation method

In a flat bottom flask, TEOS (80% by wt.) was diluted two times with ethanol and stirred vigorously for 15 minutes at room temperature. Dilute solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20% by wt.) was then added slowly with continuous stirring. The resulting solution was precipitated by the drop wise addition of ammonium hydroxide, and the pH of the solution was maintained at 10. It was then kept in oil bath at 90-100°C for 4 hr. The resulting mixed oxide precipitate was carefully filtered using vacuum pump, washed with double distilled water, until the pH of the solution decreased from 10 to 7. The content was dried at 120°C in hot air oven (Spectra Lab) for 12 hr. After drying, the oxide was ground to sieve size 100 μm in a pestle-mortar and then calcined in muffle furnace (Ambassador) at 550°C for 5 hours at ramp rate of 1°C/min. The sample synthesized by this method was referred to as SA1.

1.1.2 Sol-Gel method

The method of synthesis in this technique followed the steps similar to the co-precipitation method. But the solution is heated at 60°C for 24 hours for the formation gel upon aging. Using flat bottom flask, TEOS (80% by wt.) was diluted twice with addition of ethanol. Further, alcoholic solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20% by wt.) was then added slowly with continuous stirring. The resulting solution was converted into gel by the addition of ammonium hydroxide drop wise, and the solution was alkaline when the pH was measured as 10. It was kept in water bath at 60°C for 24 hours. The resulting gel was SAC which was carefully filtered using vacuum pump, followed by washing the contents with double distilled water, until the pH of filtrate decreased from 10 to 7. The gel was heated at 120°C in hot air oven (Spectra Lab) overnight. After drying, SAC was ground to sieve size 100 μm in a pestle-mortar and then calcined in furnace at 550°C for 5 hours at ramp rate of 1°C/min. The sample is referred as SA2.

1.1.3 Microwave synthesis

TEOS (80% by wt.) was taken in 500ml round bottom flask and diluted with dilute nitric acid. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20% by wt.) was dissolved in dilute nitric acid and mixed with the above solution of TEOS. The resulting solution was kept in microwave reactor (Raga Tech) with continuous stirring at 600 rpm; temperature was maintained at 70°C for 20 min. The reaction was exothermic and after 20 min, a white precipitate SAC is obtained, which was dried in hot air oven at 120°C overnight. Next day, the oxide was sieved and calcined at 550°C for 5 hours. This sample was referred as SA3.

2 CHARACTERIZATION

All three SACs (SA1, SA2, and SA3) were calcined at 550°C at a ramp rate of 1°C/min. The powder X-ray diffraction(PXRD) patterns were measured on Bruker D8 advance X-ray diffractometer. $\text{CuK}\alpha$ contribution was eliminated by DIFFRAC/EVA software ($\text{CuK}\alpha$ radiation with $\lambda = 1.541 \text{ \AA}$) with applied voltage 40 kV and current 40mA. The range examined was $2\theta = 15$ to 80°; the data were collected with a scan rate of 10° min^{-1} and a step size of 0.3°. The morphology of the structured oxides was evaluated by field emission scanning electron microscopy (Fe-SEM, SERON Technology, Korea) with size range 5-50 μm using 20 kV on a magnification of X1k-10k range. Fourier transform infrared spectroscopy (FTIR; Perkin Elmer) was performed to examine the linkages between silica and heterometal oxide network. The samples were prepared as KBr pastilles, with a proportion of 1% of the solids and frequency range 500-4000 cm^{-1} . The Brunauer-Emmett-Teller (BET) surface area, pore size distributions, pore volumes, and average particle size was measured by nitrogen adsorption/desorption isotherm at 75 K using accelerated Surface Area and Porosimetry System, Micromeritics, ASAP 2020. All the samples were degassed at

250°C for 6 hours, prior to actual measurements. The profile of temperature-programmed desorption of ammonia (NH₃-TPD) over the catalysts was carried out in a U type quartz reactor (id = 6 mm) packed with about 0.1 g catalyst with a Micromeritics Chemsorb 2750. The samples were pre-treated for two hours at 150°C, under argon flow of 20 ml per minute followed by cooling to room temperature in order to remove any physisorbed species on the surface of the sample. After this pre-treatment, the samples were subjected to chemisorption step using ammonia in helium (9.8%, mol/mol) flow of 20 ml min⁻¹ at room temperature, for 30 minutes. Thereafter, the system was purged with helium at room temperature for two hours. In order to remove the extra ammonia molecules, the material was treated for 30 minutes at 120°C under helium flow rate (20ml min⁻¹). This step was followed by the thermal programmed desorption analysis, in which the sample was heated from 100 to 900°C, at a rate of 10°C min⁻¹ and under helium flow (20 mlmin⁻¹). The amount of desorbed ammonia was detected with a thermal conductivity detector. The strength of the material was analyzed in terms of bulk density by pore filling method.

RESULTS AND DISCUSSION

2.1 X-ray diffraction

It was found from PXRD pattern analysis that sample SAC[SA3, as shown in Fig.1(c)] prepared by microwave synthesis possesses sharp line between 2θ range 25°-30°, which may be due to its crystalline nature; whereas other three samples (pure silica, SA1 and SA2) were observed in the range 25°– 30°, 2θ values and appear to be amorphous in nature [as shown in PXRD pattern Fig. 1 (a), (b),(d)].

2.2 SEM analysis

SEM images for all three prepared samples along with pure silica are shown in the Fig. 2. It is observed from SEM images that in case of SA1, particle size is 5μm with resolution X10K in the photograph. This may account for the binding of two metal oxides together in single particle with distinguished physical appearance in the grain size and shape, with uniformity of all particles. Image for SA2 shows the fine grain size as 5μm at resolution X10K with uniform particle thickness. Uniformity in grain size and agglomeration could be a result of sol-gel synthesis, which might have helped in the binding the particles well.

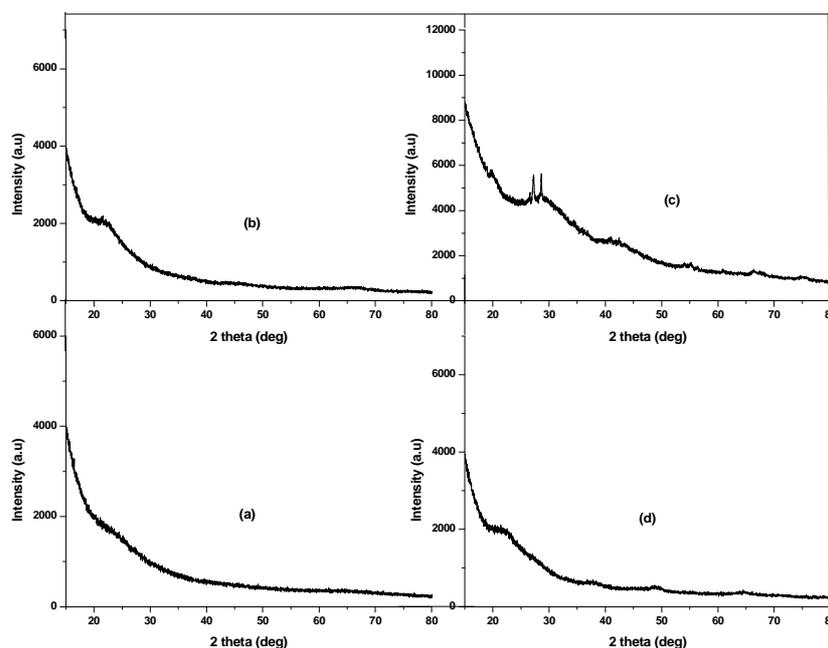


Figure 1 XRD pattern of (a) Pure silica, (b) SA-1, (c) SA-3, (d) SA-2

SEM image of SA3 indicated particle size as 50μm with resolution X1.0K. The particles are small and spherical in shape and uniform in size. All as prepared samples (SA1, SA2, and SA3) are mesoporous in physical nature.

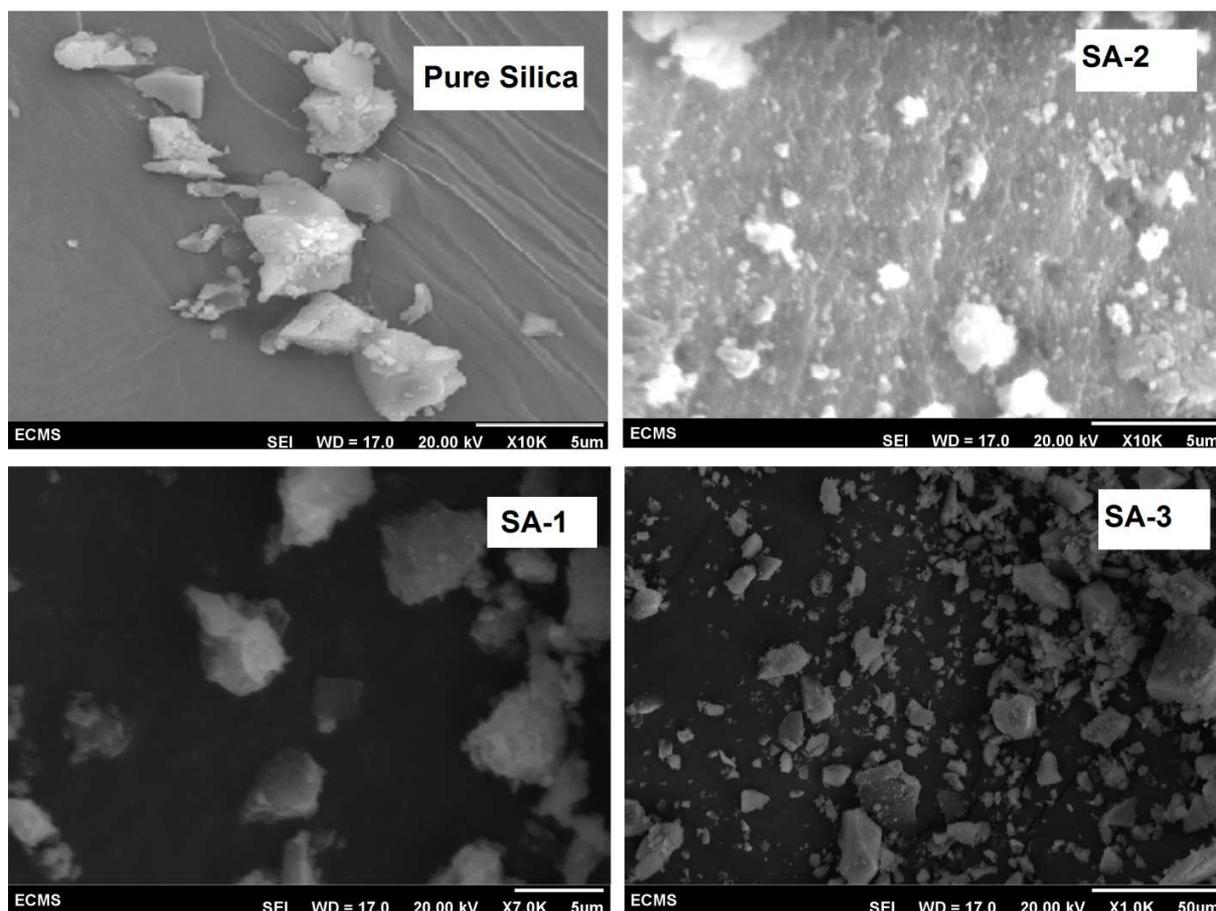


Figure 2 SEM photographs of samples

2.3 N₂ adsorption and desorption

Figure 3 shows the N₂ adsorption-desorption isotherms for SAC by various routes. Type IV isotherms were obtained for all the samples [17]. Limiting adsorption at high P/P_0 was not exhibited and the isotherms comprised of H3 type hysteresis loops. This suggested the existence of aggregates of plate like particles creating slit shaped pores. Results indicate the formation of mesoporous samples, which is evident by the observation that the volume of nitrogen adsorbed did not significantly increase until at relative pressures (P/P_0), position of inflection points exceeding 0.4[18]. The existence of conspicuous hysteresis loops at high relative pressures also indicates the presence of mesoporous material, being related to capillary condensation associated with large pore channels[19]. Fig. 4 describes the pore size distribution (PSD) calculated from desorption branch of the isotherm. The PSD of the final products indicate that SAC samples synthesized under normal laboratory conditions have wider PSD than that synthesized under microwave irradiation. The intercalation of oxides and reduction of particle size to nano range could help in achieving high surface area with appreciable pore volume. Both surface area and pore volume of SACs followed the same order: SA3 (453m²/g) > SA1 (345m²/g) > SA2 (324m²/g); and SA3 (0.70cc/g) > SA1 (0.62cc/g) > SA2 (0.35cc/g) respectively. Maximum surface area in case of microwave synthesis can be attributed to the digestion of the reaction mixture under high intensity microwave irradiation. This could help in sufficient dispersion of particles, resulting in an appreciable decrease in particle size, leading to the generation of product with very high surface area and pore volume. Surface area, pore volume, average pore diameter, average particle size, total acidity, and bulk density of the samples is given in table-1.

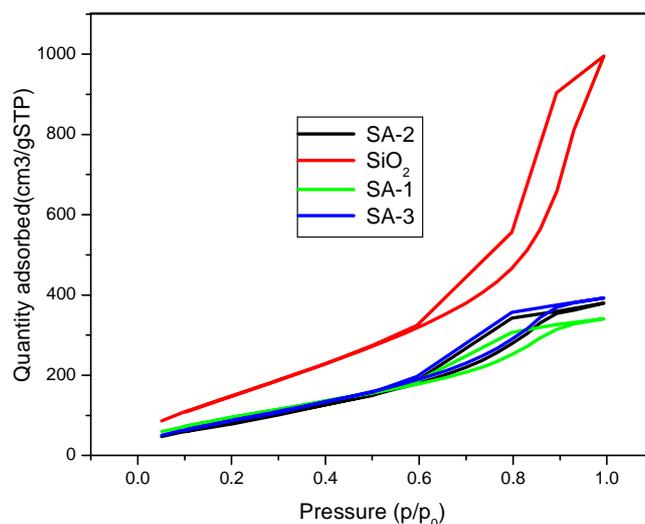


Figure 3 Nitrogen adsorption/desorption Isotherm of Samples

Table 1: Physico-chemical parameters of silica alumina composite

Sample	S_A (m ² /g)	V_P (cc/g)	D_P (nm)	S_P (nm)	A_T (mmol/g)	D_B (g/cc)	Crystallinity
Pure SiO ₂	578	1.7	10.0	11.0	0.1	0.2	Amorphous
SA1	345	0.620	4.34	19.01	0.314	0.65	Amorphous
SA2	324	0.35	3.67	18.50	0.374	0.69	Amorphous
SA3	453	0.70	6.50	13.83	0.392	0.56	Crystalline

S_A : Surface area; V_P : Pore volume; D_P : Average pore diameter; S_P : Average particle size; A_T : Total acidity; D_B : Bulk density

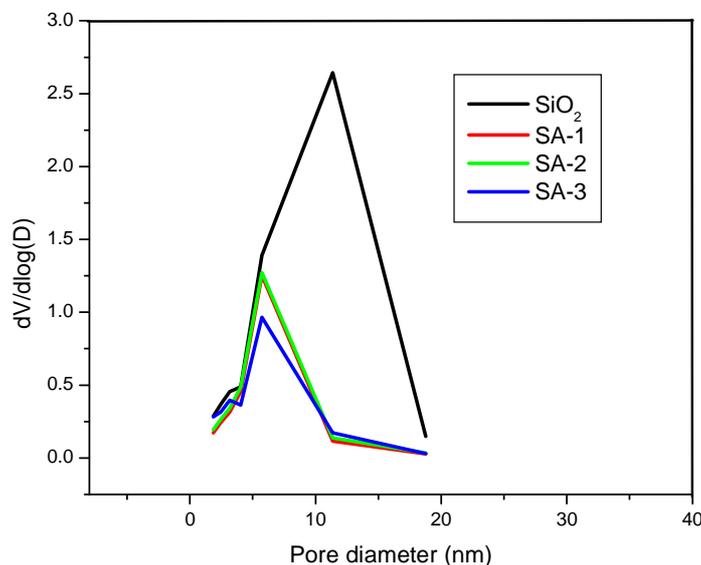


Figure 4 Pore size distributions of samples

2.4 FT-IR spectral Analysis

FTIR spectra for all the three samples are presented in Fig.5(b),(c),(d) along with pure silica Fig.5(a). A broad peak at 3459 cm⁻¹ in all the spectra correspond to vibrational peak of -OH group with variable intensities, but in the case of FTIR for SA3 [Fig.5(c)], this broad peak has less intensity which may due to heating the reaction mixture in microwave reactor while preparing the mixed oxide at 70°C. Sharp peak at 1632cm⁻¹ in the spectrum of pure silica

marks the presence of H-O-H bending vibration of water. Peak at 1111cm^{-1} reflects asymmetric stretching of Si-O-Si; 820cm^{-1} indicates symmetric stretching of Si-O-Si. Decrease in the intensity of 1111cm^{-1} in structured oxides indicates the involvement of silica in linkage with other metals. Among the FTIRs of mixed oxides, occurrence of peak at 1088cm^{-1} corresponds to Si-O-Al bonding in Si-Al oxide. This peak has different intensity in the FTIR of pure silica and the samples prepared by sol-gel and co-precipitation technique. Synthesis of well mixed composite is evident from the FTIR of SA3 reflecting the sharp peak due to Si-O-Al (1088cm^{-1}) as compared to other samples. The peak at 1092cm^{-1} is the characteristic of Si-O-Si vibration, while the shoulders appearing at high and lower side of this absorption band indicate the presence of Si-O-Al bonds through cross-condensation of alumina and silica precursors[20-26].

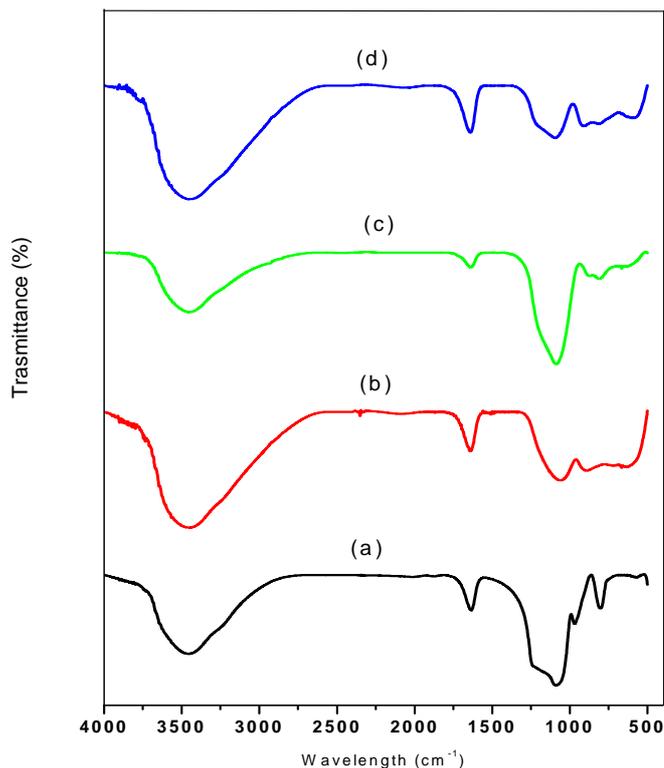


Figure 5: FTIR Spectra of (a) Pure silica (b) SA-1 (c) SA-3 (d) SA-2

2.5NH₃- TPD

SACs were subjected to temperature program desorption of ammonia. The concentration and strength of acid sites was evaluated by NH₃-TPD. During this process, a particular amount of NH₃ is desorbed per gram of sample, which is an indicative of its acidity. In NH₃-TPD profile, peaks generally are distributed into two regions, high temperature (HT) region ($T > 400^\circ\text{C}$) recognizing desorption of ammonia from strong acid sites and low temperature (LT) region ($T < 400^\circ\text{C}$) recognizing desorption of ammonia from weak acid sites [27,28].

TPD profile for all SAC samples (SA1, SA2 and SA3) were taken from $100\text{--}900^\circ\text{C}$ (Fig. 6). All the samples showed peaks between 100 to 500°C . The results demonstrate the presence of acid sites of different strength in these solids. In table 2 the desorption peaks of TPD profiles located at $100\text{--}200^\circ\text{C}$, $200\text{--}400^\circ\text{C}$ and $400\text{--}650^\circ\text{C}$ can be assigned to weak, moderate and strong acid sites, respectively [29]. Peak above 500°C corresponded to the decomposition of strongly absorbed ammonia.

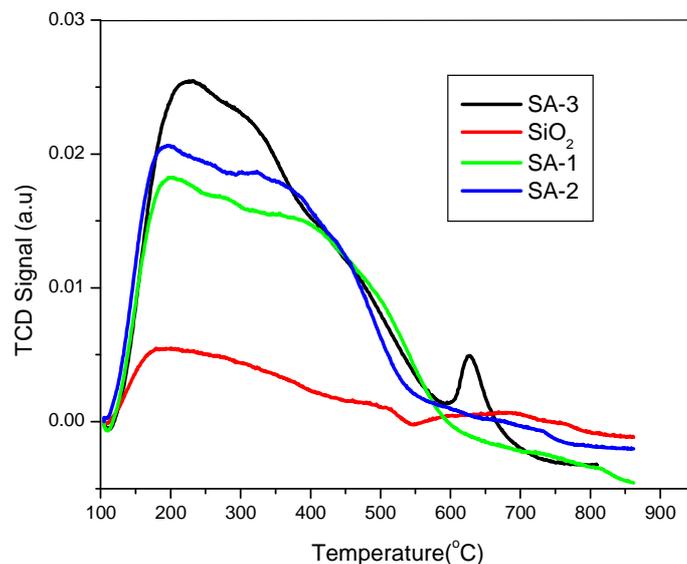
Figure 6: NH₃TPD profile of samples by ammonia absorption /desorption methods

Table-2: Acid sites in the samples

Sample	NH ₃ desorbed			Total volume desorbed (ml)	
	100-200°C	(Weak sites)	200-400°C (Moderate sites)		400-450°C (Strong sites)
SA1	0.468		5.92	0.660	7.04
SA2	0.662		6.028	1.78	8.38
SA3	0.80		6.504	1.50	8.80
Pure SiO ₂	0.25		1.90	0.35	2.50

Results show different extent of ammonia desorbed for the sample obtained by various routes. This indicated total acidity in the samples (Table-1).

Pure SiO₂ contained 0.35mmol/g at STP strong acid sites. While the SAC catalyst prepared in over study contained 0.660–1.78mmol/g

CONCLUSION

Combination of mixed composite is a good choice as catalyst for the reactions requiring high surface area and appreciable acidity. Silica-alumina mixed oxides have been synthesized by co-precipitation, sol-gel and microwave methods. All the methods produced samples with high surface area and pore volume, viz. 324-453m²/g and 0.35-0.70cc/g respectively; however microwave method can be suggested as the best to generate maximum surface area among the three, which is the foremost and very important requirement for a catalytic material. Also it could help in producing crystalline sample with high pore volume and acidity (0.392mmol/g). Samples have been synthesized as nano-composites with average particle size (11-19nm). FTIR results showed the interlinkage between Si-O-Al due the condensation of alumina and silica precursors. The prepared composite samples can be tried over a variety of reactions requiring appreciable acidity and the conditions can be optimized as per demand of the reaction.

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