

SURFACE AREA: AN EXPLORATORY TOOL**K. Mantri* and I. Vaidya***Department of Quality Assurance,
Dr. L. H. Hiranandani College of Pharmacy, Ulhasnagar- 421003, India.**(Received on: 22-06-14; Revised & Accepted on: 30-06-14)***ABSTRACT**

Surface area is a ubiquitous term used in the field of mathematics, material and biological sciences. Specific surface area of material is an important physical parameter and influences many aspects of product performance such as the hiding power of pigments, the activity of catalysts, the taste of food, the potency of drugs and the bioavailability of drugs. A variety of classical and advanced instrumental measurement methods to calculate specific surface area are available in the literature. The review gives glimpse of these methods and focuses mainly on important applications of specific surface area in the pharmaceuticals, catalysis, hydrogen storage and electronics.

Keywords: surface area, pharmaceuticals, catalyst.

INTRODUCTION

Surface area is a generalized term and it has significance in mathematics and material science. Powder surface area has got numerous applications. Whenever matter is divided into smaller particles, new surfaces must be produced with a corresponding increase in surface area. In addition to particle size, the particle shape contributes to the surface area of the powder. All particulate matter possesses geometry and, therefore, surface area between these two extremes. Attempts to measure surface area will give results significantly less than the true value, or greater depending upon particle shape, surface irregularities and porosity. At best, surface areas calculated from particle size will establish the lower limit by the implicit assumptions of sphericity or some other regular geometric shape, or by ignoring the highly irregular nature of real surfaces.¹

The specific surface area is the area of solid surface material which actually determines the accessible (or detectable) area of solid surface per unit mass of material. Specific surface area is usually deduced from measured quantities that must be interpreted using simplified models of the measurement process. Consequently, the recorded value depends inherently on the validity of the assumptions used in the model.²

Calculation for specific surface area

The "specific surface area" is the surface area per unit volume (S_v) or per unit weight (S_w) of material.³

$$S_v = \frac{\text{surface area of particles}}{\text{Volume of particles}}$$

$$S_v = \frac{n\alpha_s d^2}{n\alpha_v d^3} = \frac{\alpha_s}{\alpha_v d} \quad (1)$$

where, n = number of particles

α_s = surface area factor

α_v = volume factor

d = diameter of particle

The surface area per unit weight is therefore,

$$S_w = S_{w\rho} \quad (2)$$

Where, $\rho = v$ true density of particle

Corresponding author: K. Mantri*, E-mail: kirtimantri23@gmail.com

METHODS FOR DETERMINING SURFACE AREA

The surface area of a powder sample can be computed from knowledge of the particle size distribution. Two methods are commonly available that permit direct calculation of surface area. In the first method, the amount of gas or liquid solute that is adsorbed onto the sample of a powder to form a monolayer is a direct function of the surface area of sample. The second method takes into account the fact that rate at which gas or liquid permeates a bed of powder is related, to the surface area exposed to the permeant.³

The classical methods known are

- Adsorption Method
- Air Permeability Method
- BET Method
 - i) Multiple point Method
 - ii) Single point Method

Newer methods:

Methane adsorption

Computed tomography

Laser Desorption

Small angle X-Ray scattering

Other Surface Area Methods

- **GAS ADSORPTION : HARKINS AND JURA RELATIVE METHOD**
- **IMMERSION CALORIMETRY: HARKINS AND JURA ABSOLUTE METHOD**

Chemical and physical processes, such as heterogeneous chemical reactions, light scattering, and metamorphism occur in the natural snowpack. To model these processes in the snowpack, the specific surface area (SSA) is a key parameter. In this study, two methods, computed tomography and methane adsorption, which have intrinsically different effective resolutions – molecular and 30 μ m, respectively–were used to determine the SSA of similar natural snow samples. Although the two techniques used are based on two different physical concepts, the correlation factor between both methods was found to be 1.03(\pm 0.03), for SSA values ranging between 50 and 700 cm² g⁻¹.

ADSORPTION METHOD

Particles with large specific surface are good adsorbents for the adsorption of gases and of solutes from solution.³ In determining the surface of the adsorbent, the volume in cubic centimeters of gas adsorbed per gram of adsorbent may be plotted against the pressure of the gas at constant temperature to give a Type II isotherm.

Some new instruments have replaced the older vacuum system constructed of networks of glass tubing. These required long periods of time to equilibrate and were subject to leakage at valves and break in the glass lines. The sensitivity of the new instrument is such that small powder samples may be analysed. The new systems versatility allows the use of a number of individual gases or mixture of gases as adsorbates over a range of temperatures.

AIR PERMEABILITY METHOD

The major resistance to the flow of a fluid, such as air, through a plug of compacted powder is the surface area of the powder. The greater the surface area per gram of powder, S_w , the greater the resistance to flow. Hence permeability, for a given pressure drop across the plug, is inversely proportional to specific surface. The measurement of the permeability provides a means of estimating surface area.³

A plug of powder may be regarded as a series of capillaries whose diameter is related to the average particle size. The internal surface of the particles is a function of the surface area of the particles. According to Poiseuille' sequeation:

$$V = \pi d^4 \Delta p t / 128 l \eta \quad (3)$$

Where, V= volume of air flowing through a capillary of internal diameter d

l= length

t= seconds under a pressure difference of p

The viscosity of the fluid (air) in η poise. In practice, the flow rate through the plug or bed, is also affected by (i) degree of compression of the particles and (ii) the irregularities of capillaries. The more compact the plug, the lower the porosity which is the ratio of the total space between the particles to the total volume of plug. Because of the simple instrumentation and the speed with which determinations can be made, permeability methods are widely used for specific surface determinations, especially when the aim is to control batch to batch variations.

TOMOGRAPHY

In this method modified X-ray computer tomograph, with a microfocus X-ray source emitting a white spectrum (45 kV acceleration voltage) is used to scan the samples. A 180° rotation of the sample is divided into 1000 steps. At each angular step, a 1024×128 CCD detector captures the absorption signal during an integration time of the order of ms, and averaged over two such intervals in order to reduce the noise. The apparatus resides in a cold room at -15°C. Along with each adsorption measurement, two or three tomograms are taken. After scanning, a subvolume was extracted from the reconstructed image.

LASER DIFFRACTION

Laser diffraction (LD) is the method most commonly used by the cement industry to quantify the particle size density (PSD) of a powder. The method is simple to perform and can be automated. The LD method involves the detection and analysis of the angular distribution of scattered light produced by a laser passing through a dilute dispersion of particles. The total scattering or diffracted light pattern is mathematically inverted, using Fraunhofer or Mie scattering theory, to yield the particle size distribution of spheres that would give the equivalent scattering pattern. The surface area is calculated from the diameter distribution of the spherical particles. In general, the LD method requires that the particles be dispersed either in liquid (suspension) or in air (aerosol). The former is commonly referred to as the “wet” method (LD-W), while the latter is termed the “dry” method (LD-D).

SMALL ANGLE SCATTERING (SANS and SAXS)

Small-angle scattering is a powerful tool for characterizing complex micro-structures. An intense beam of either neutrons (SANS) or x-rays (SAXS) is passed through the specimen, and a small component is scattered out of the incident beam direction by interactions with microstructural features within the bulk of the material. For cement paste and similar porous materials, the resulting scattering profile, which is the intensity of scattered neutrons or x-rays as a function of scattering angle, is effectively a form of Fourier transform of the solid/pore microstructure. It can be used to determine, for example, size distributions and volume fractions of microstructural features, fractal components within the microstructure, and the total surface area. Reported SAXS surface areas are significantly higher than SANS surface areas

APPLICATIONS

1.1 Magnesium Stearate

i) Lubrication Property

Magnesium stearate is widely used as a lubricant in the area of pharmaceutical solid dosage form. This is mainly due to its ability to decrease friction between a tablet and die wall during the ejection stage of the compression process.^{7,8}

To improve the lubrication potential, two grades of magnesium stearate (MS) blended with a mix of dicalcium phosphate dihydrate and microcrystalline cellulose and lubrication potential was studied. Dicalcium phosphate being a brittle material, the fragmentation under confined loading generates new surfaces, on which the lubricant particles can be loaded. Micro crystalline cellulose which consolidates by plastic deformation, remains lubricant-sensitive. An increase in mixing time with Magnesium stearate led to increased surface distribution, which resulted in favorable particle rearrangement and a reduction in ejection force. Hence, the better performance of sample A can be attributed to its superior solid-state properties which is given in Table. 1

TABLE – 1: Comparison of surface area grades of magnesium stearate.

SAMPLE	PARTICLE SIZE (μm)	SURFACE AREA (m^2/g)
A	1.12 μm	6.63
B	1.38 μm	1.66

Solid-state properties of the Magnesium stearate samples—particle size, and specific surface area—have an influence on the lubrication performance. In British Pharmacopoeia the specific surface area for magnesium stearate is p/p_0 range of 0.05 to 0.15. sample outgassing = 2 h at 40° C.⁹

ii) Effect of Temperature and Humidity

The specific surface area is a parameter apparently affecting the lubricating properties of magnesium stearate. Another reason for the different physical properties is the moisture content and the hydration state of the magnesium stearate samples. Since all samples are usually degassed before BET analysis, the other reason may be the degassing temperature. In one of the study three forms of magnesium stearate such as magnesium monohydrate, magnesium dihydrate and magnesium trihydrate were used and specific surface area was measured at different time intervals. The specific surface area for all the samples found to decrease with increasing degassing temperature. Although magnesium stearate is known to be hydrophobic, the results show that the samples are slightly hydrophilic; the moisture uptakes vary from 1% to 3%. In conclusion, the physical properties of the magnesium stearate samples changed after moisture treatment.^{10,11}

1.2) Drug Delivery

Inhalation Efficiency

Micronized pranlukast hydrate is antiasthmatic agent has poor inhalation and micromeritic properties due to their strong adhesiveness. For pulmonary delivery system lactose is used as carrier¹². To finalize the grade of lactose the help of surface area parameter was found to be useful. Various Crystalline forms of carrier lactose were taken and the surface area was determined for different forms which are tabulated in Table 2.

Table - 2: Comparison of specific surface area of various lactose grades

Sample	Crystalline form	Specific surface area (m ² /g)		Surface roughness ^c
		Permeametry method ^b	Adsorption method ^a	
A	α -Monohydrate	0.202±0.002	0.233±0.007	1.13±0.01
B	α -Monohydrate	0.206±0.003	0.234±0.012	1.16±0.03
C	α -Monohydrate/amorphous	0.242±0.015	0.232±0.003	1.13±0.02
D	β -Anhydrate/ α -anhydrate	0.265±0.002	0.286±0.014	1.16±0.03
E	α -Monohydrate	0.348±0.001	0.362±0.029	1.33±0.08
F	Amorphous	0.146±0.010	0.139±0.002	1.08±0.01
G	α -Monohydrate/ β -anhydrate	0.174±0.005	0.230±0.004	1.14±0.02

a Data are represented with mean \pm S.D. ($n=2$).

b Data are represented with mean \pm S.D. ($n=3$).

c Data are represented with mean \pm S.D. ($n=10$).

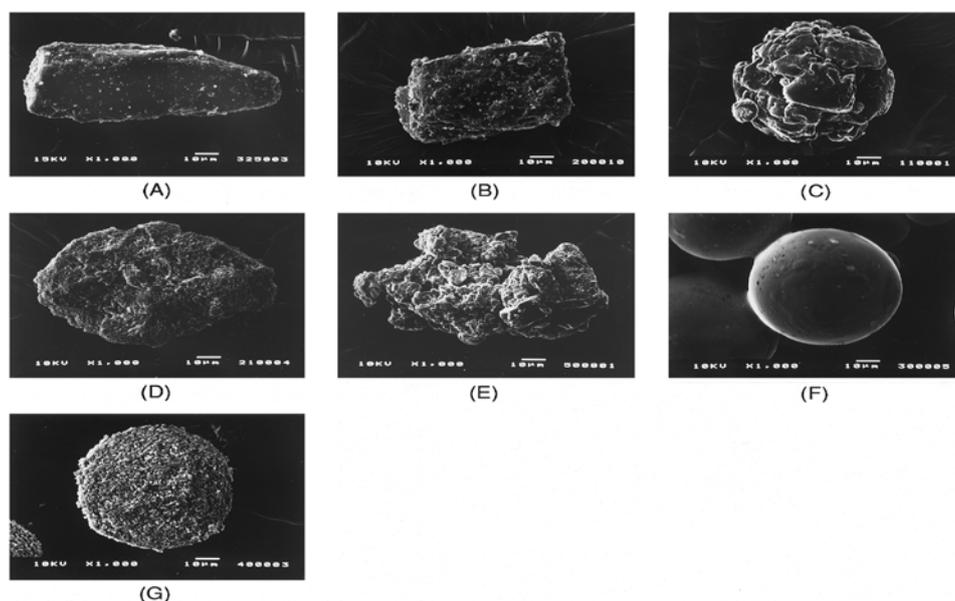


Fig – 1: Sem Of Carrier Lactose

The surface topographies of carrier lactose were described more quantitatively with specific surface area and surface roughness in Table 2. The specific surface areas determined by gas adsorption method were slightly larger than those by permeametry method. This finding indicated that the surface area of carrier lactose was determined by the surface topography. The specific surface areas of F and G forms were smaller than the others, whereas that of E form was largest among the carrier grades. The order of surface roughness of carrier lactose was well corresponded to that of specific surface area. In conclusion, the design of surface morphology, sample G has fairly large surface area with microscopically increased surface roughness, was found to be desirable to improve the inhalation efficiency of dry powder inhalation.

Another example for dry powder inhalation efficacy is salbutamol sulfate by using polycaprolactone microparticle as carrier¹³.

1.3) Nanoparticles

In the pharmaceutical industry, a large numbers of drugs are insoluble or poorly soluble in water and drugs sparingly soluble in water are quite often highly soluble in organic solvents. The bioavailability (the percentage of the drug absorbed compared to its initial dosage) is limited by this insolubility. The drug must first be dissolved in order to be absorbed. Dissolution rate is a function of the surface area of the particles and solubility¹⁴. The surface area can be determined through the control of the particle size. Therefore, the bioavailability of the water insoluble drugs can be improved by reduction in their particle size and increase in surface area.

Reducing drug particles size is an effective and widely used approach to speed up dissolution by enlarging the effective surface area. According to Noyes–Whitney equation, the dissolution rate is proportional to the surface area exposed to the dissolution medium. Dissolution profile of raw ibuprofen and precipitated nanoparticles at room temperature is illustrated in Fig. (5), respectively.

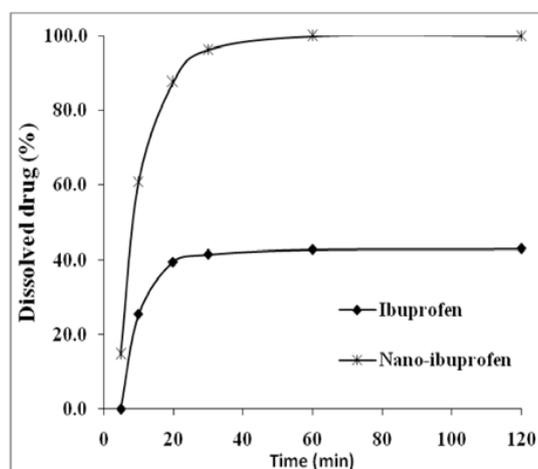


Fig. – 2: Dissolution profile of raw ibuprofen and drug nanoibuprofen

The dissolution rate of ibuprofen nanoparticles is 2.33 times that of ibuprofen. According to Noyes–Whitney equation, the solid dissolution rate is directly proportional to its surface area exposed to the dissolution medium. The accelerated dissolution for ibuprofen nanoparticles could thus be mainly ascribed to their greater surface area (5.6- 9.3 m²/g) in comparison with raw drug (0.11- 0.45 m²/g). This indicates that the acceleration of drug dissolution for nanoparticles occurs mostly in the first 30 min and is 2.33 times the raw drug.

Another example for solubility and dissolution enhancement by nanoparticles is Meloxicam¹⁵.

1.4) Vaccines

Vaccines often are not sufficiently stable in aqueous solution to allow distribution and storage, particularly at room temperature. Therefore, solid dosage forms are produced by drying, typically freeze-drying. In a vaccine product, the “active ingredient” can be live attenuated, genetically modified live, inactivated, synthetic peptide-based, nucleic acid or subunit vaccine. Because of the low stability of some vaccines in solution and the high cost of vaccines, drying of vaccine formulations is becoming a common practice. Additionally, the high cost of preservation of vaccine solutions and suspensions due to stringent cold storage requirements is reduced by drying. Drying methods based on the principle of foaming and rapid evaporation of water (foam drying) were developed in the 1960s for preservation of vaccines and bacteria. Now, these methods or modifications of these methods such as Xerovac, foam freeze drying or vacuum drying are currently under re-investigation as alternate drying methods¹⁶.

Powders produced by different drying methods have different physical properties. Differences in powder properties arise from differences in moisture content, particle size, particle morphology, powder density, specific surface area, surface composition, thermal properties, and other properties. For example, dried particles of a vaccine formulation for needle-free injections are required to have a particle size < 70 μm to avoid tissue injury, narrow particle size distribution for uniform acceleration and penetration in the tissue, and high density for efficient acceleration by helium gas. All

these attributes can be achieved by using spray coating or spray freeze drying. Another potentially important factor is that different drying methods result in dried powders of varying specific surface area (SSA).

Results for specific surface area measurements on all preparations are reported in Table 3.

Table – 3: Effect of Moisture Content of vaccine on Specific Surface Area (SSA)

	Treatment	Moisture Content (% w/w)	SSA (m ² /g)TSDa
1:100 (Vaccine: Sucrose)	Freeze dried	1.0	1.42±0.03
	Annealed/ Freeze dried	2.2	0.71±0.03
	Spray dried	1.0	2.80±0.07
	Foam dried	2.2	0.13±0.02
1:100 (Vaccine: Sucrose) with Pluronic F-68	Freeze dried	0.8	1.15±0.02
	Annealed/ Freeze dried	1.9	0.64±0.03
	Spray dried	1.9	1.26±0.03
	Foam dried	2.3	0.10±0.01

a SD: standard deviation

In surfactant-free preparations, specific surface area was highest in spray dried preparation and extremely low with the foam dried samples. Intermediate values for specific surface area were observed with the freeze dried preparations.

Upon addition of the surfactant, specific surface area of spray dried and freeze dried preparations decreased and were comparable. Again specific surface area was less with the preparation annealed prior to freeze-drying and was extremely low with the foam dried formulation. Improvement in stability with foams was associated with very low specific surface area.

1.5) Mesoporous Material for Drug Delivery

Several groups have reported the use of mesoporous materials as drug carriers. Among the drug supports, the mesostructured silica-based materials present some advantages: biocompatibility, tunable pores size and morphology, large specific surface area, high pore volume that allow a good adsorption of biologic active molecules. Al-containing mesoporous materials present stability and enhanced acidity towards silica and can be applied as drug carriers¹⁷. Mesoporous aluminosilicates AIMCM41 were synthesized by using tetraethylorthosilicate as silicon source, and different aluminum precursors either sodium aluminate or aluminum *sec*-butoxide.

TABLE - 4: Surface area of mesoporous aluminosilicates

SAMPLE	SPECIFIC SURFACE AREA(m ² /g)
Sample A	993 m ² /g
Sample B	595 m ² /g

Scanning electron microscopy investigation of sample A showed primary nanometric spherical particles that have the tendency of spherical agglomerates formation with uniform size and less than 100 nm (Fig. 6A). The scanning electron microscopy investigation of sample B proves a small tendency of spherical agglomerates formation with 50-100 nm diameter and a narrow size distribution (FIG 6B).

All aluminosilicate samples obtained are good quality MCM-41 mesoporous materials. AIMCM41 sample obtain from aluminum tri *sec*-butoxide as metallic source has higher values for specific surface area. The good textural features of this AIMCM41 sample, comparable with those of commercially available silica MCM41 recommend this as biological active molecule carrier in drug controlled release system.

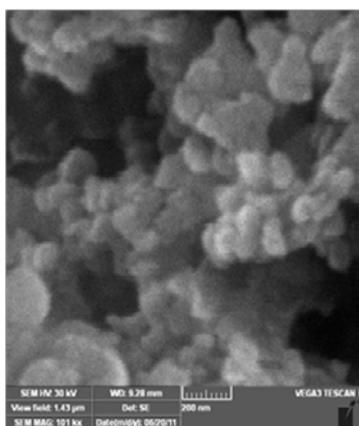


Fig. - 3a: Sem Micrographs Sample (A)

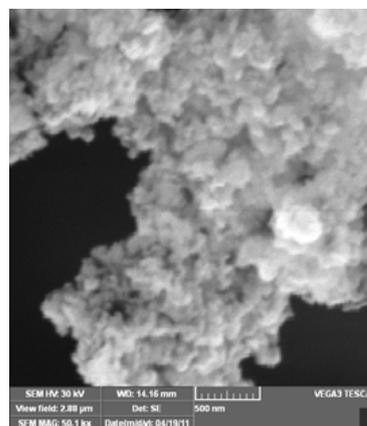


Fig. - 3b: sem Micrographs Sample (B)

Mesoporous materials are used for oral drug delivery such as Ranitidine, Ibuprofen, Furosemide and Griseofulvin¹⁸.

1.6) Mesoporous Material for Adsorption of Proteins

Mesoporous molecular sieves (MMS) are used as catalysts or adsorbents for industrial separation processes. In particular, their high surface area ($\geq 1000 \text{ m}^2 \text{ g}^{-1}$) and tuneable narrow pore size distributions in the mesoporous region (2 – 50 nm), give them substantial potential for size exclusion separations of large molecules such as proteins¹⁹. In addition, their surfaces may be functionalised by binding organic ligands to the silanol groups on the surfaces of the pores or incorporating such ligands into the porous structure through co-condensation, to enhance their selective adsorption of a target molecule.

Mesoporous molecular sieves were used for adsorption of proteins and enzymes. It shows its potential benefit for separation of proteins.

1.7) OTHER APPLICATIONS

The other applications of surface area such as it can be used in Cement Industries, Adhesives, Electronics, Catalyst, Hydrogen storage, Supercapacitors. some of them are explained below.

i) Hydrogen Storage

The use of hydrogen as a fuel and the development of a hydrogen economy have been suggested as means to decrease our dependency on petroleum products worldwide. However significant technological hurdles need to be overcome and one such hurdle is the development of safe, compact, and high capacity storage systems for molecular hydrogen. Three polymers have been prepared from 6,5 -tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane copolymerized in bulk with tetrafluoroterephthalonitrile, hexachlorohexaazatrinaphthylene, and cyclotricatechylene to afford materials with intrinsic porosity having BET surface areas ranging from 760 to 830 m^2/g . Table 5 lists only those polymers that had a surface area exceeding 500 m^2/g as calculated from nitrogen adsorption using the BET equation. Although the small difference in surface areas between adsorbents may not fully account for the rather large difference in hydrogen adsorption, the results appear qualitatively more reasonable since the resin with a higher apparent surface area absorbs more hydrogen²⁰.

Table – 5: List of Commercial Resins, Their Properties, and Their Ability to Store Hydrogen

Type	Composition	Surface area (m^2/g) <i>a</i>		H_2 capacity (wt %) <i>b</i>
		<i>a</i>	<i>b</i>	
1	poly(styrene-co-divinylbenzene)	1060	425	0.8
2	poly(styrene-co-divinylbenzene)	770	336	0.6
3	poly(divinylbenzene-co-ethylenedimethacrylate)	460	247	0.5
4	polydivinylbenzene modified with polyethyleneimine	570	290	0.5
5	poly(divinylbenzene-co-4-vinylpyridine)	510	254	0.5
6	poly(styrene-co-divinylbenzene)	940	573	1.2
7	poly(styrene-co-divinylbenzene)	1206	664	1.3
8	poly(styrene-co-divinylbenzene)	810	377	0.7
9	hypercrosslinked polystyrene	840	576	1.3
10	amine functionalized hypercrosslinked polystyrene	600	477	1.1
11	sulfonated hypercrosslinked polystyrene	370	266	0.7

(a) *a* Calculated from nitrogen adsorption using the BET equation

(b) Hydrogen adsorption using the Langmuir equation

(c) *b* Hydrogen storage capacity at a pressure of 0.12 MPa.

ii) Catalytic Activity

1) Tin oxide has been more commonly used as a catalyst for the oxidation of organic compounds. In most of its applications, high surface area metal oxides such as SnO_2 are favorable and preferred due to high number of surface active groups. Tin (IV) chloride tetrahydrate ($\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$), Ammonium hydroxide (NH_4OH 25%), Sodium hydroxide (NaOH) and ultra pure water were used to prepare tin oxide nanoparticles by sol-gel method. Ammonia solution was added to the mixture of tin (IV) chloride and ultra pure water under controlled feed rate and constant stirring. The p^{H} values range between 1 to 10.2 and reaction temperature were varied between 30 to 90⁰ C. A study on the effect of ammonia concentration, ammonia feed rate and reaction temperature on the particles size, particles distribution and surface area of tin oxide nanoparticles using sol-gel method. The catalytic activity of tin oxide nanoparticles for the hydrogenation reaction of styrene to produce ethyl benzene was also investigated^{21,22}.

Effect of ammonia concentration on the synthesis of tin oxide nanoparticles

The study on the effect of ammonia concentration on tin oxide nanoparticles was carried out by varying the concentration of ammonia (from 1.07 to 10.67 M) while the feed rate of ammonia and reaction temperature were kept constant at 0.1 mL min⁻¹ and 30⁰, respectively. Table 6 shows the mean particle sizes and surface area of SnO₂ particles using different ammonia concentration. Consistently, the increase in particle sizes is followed by the decrease in surface area. As the concentration of ammonia varies from 1.07 to 10.67M, which result in the increase of the pH from 1 to 10.2, the particle size increases marginally from 4.2 to 5.6 nm. Meanwhile, the surface area dropped from the highest, 114 to 76 m² g⁻¹.

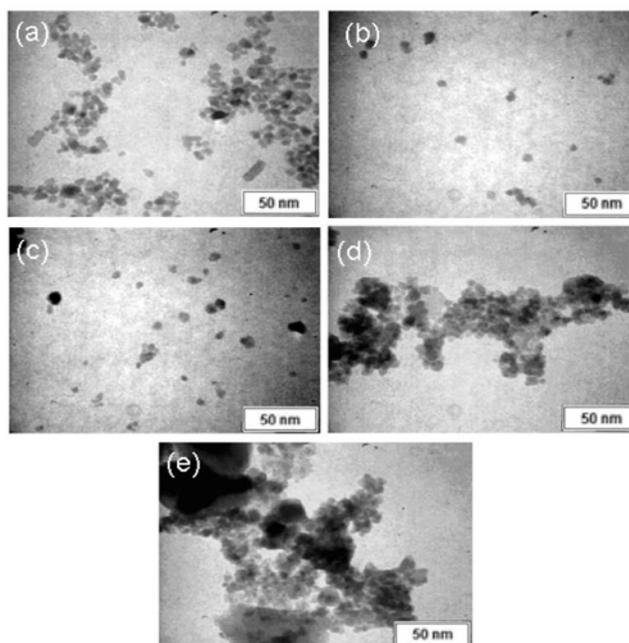


Fig. – 4: TEM micrographs of SnO₂ at different concentration of ammonia (a) 1.07 M, (b) 3.20 M, (c) 5.34 M, (d) 7.48 M and (e) 10.67 M. [Scale bar: 50 nm]

Table-6: Particle sizes and BET surface area of SnO₂ samples synthesized using different ammonia concentrations at 30⁰ C 0.1 mL min⁻¹ feed rate.

Sample	NH ₃ [M]	p ^H	Particle size(nm)	Surface area m ² g ⁻¹
BD1	1.07	1.0	4.2±0.9	114
BD2	3.20	8.7	4.6±1.1	111
BD3	5.34	9.7	4.7±1.3	89
BD4	7.48	9.9	5.4±1.3	88
BD5	10.67	10.2	5.6±1.8	76

The particles showed better distribution when the concentration of ammonia is increased up to 5.34 M. However, a further increased in the concentration of ammonia results in high particle agglomeration believed to be due to excessive generation of primary particles at super saturation state.

Effect of ammonia feed rate on the synthesis of tin oxide nanoparticles

The effect of ammonia feed rate on particle size and surface area of the tin oxide nanoparticles was studied and is given in Table 7. Fig8. shows the TEM images of SnO₂ nanoparticles obtained with feed rate from 0.1 to 0.01 ml min⁻¹ constant temperature of 30⁰ C and concentration of ammonia of 3.20M.

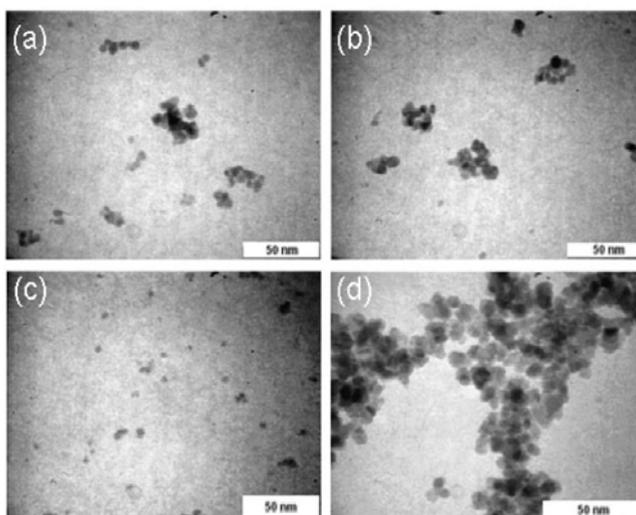


Fig. – 5: TEM micrographs of SnO₂ at different ammonia feed rate (a) 0.1 mL min⁻¹, (b) 0.05 mL min⁻¹, (c) 0.017 mL min⁻¹ and (d) 0.01 mL min⁻¹. [Scale bar: 50 nm]

Table-7: Particle sizes and BET surface area of tin oxide using different ammonia feed rate. Ammonia concentration: 3.20 M and reaction temperature 30⁰C.

Sample	NH ₃ feed rate [mL min ⁻¹]	Particle size (nm)	Surface area (m ² g ⁻¹)
BF1	0.100	4.5±1.7	111
BF2	0.050	4.4±1.0	95
BF3	0.017	4.0±0.9	99
BF4	0.010	4.7±1.1	88

In this study, slower ammonia feed into solution resulted in smaller and highly dispersed particles as shown in Table 7. However, too slow of ammonia feed rate, 0.01 mL min⁻¹, causes the formation of bigger particle, 4.7 nm compared to only 4.0 nm. The increases of the particle size is believed to be due to the aggregation of the particle (Fig. d) whereby smaller and less stable particles were deposited on more stable particles to form larger particles. In general, the surface area of tin oxide decreases when slower NH₃ feed rate is used.

Effects of reaction temperature on the synthesis of tin oxide nanoparticles

Temperature is known to be one of the most important parameter which influences particles size and their distributions. In this study, the experiment was carried out by varying the reaction temperature from 30 to 90⁰C, while the concentration of ammonia and its feed rate were kept constant at 3.20 M and 0.1 mL min⁻¹ respectively. The higher temperature favors a fast hydrolysis reaction and results in high supersaturation which also can be attributed to high nucleation rate. This will lead to the formation of a large number of small nuclei and eventually lead to the formation of small particles. Consistently, the surface area of the samples is larger when higher reaction temperature is used.

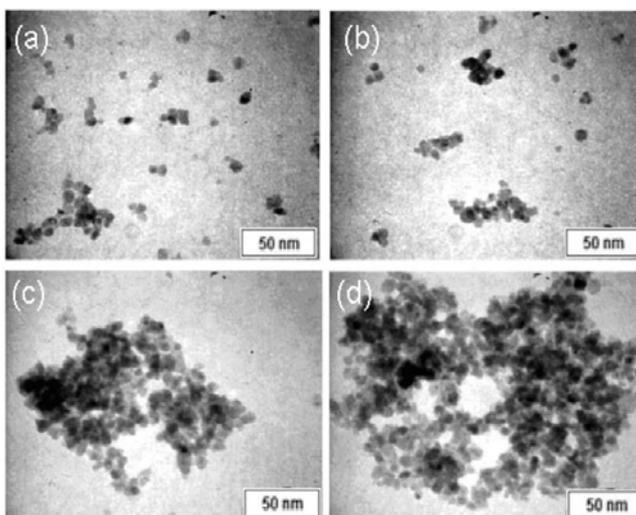


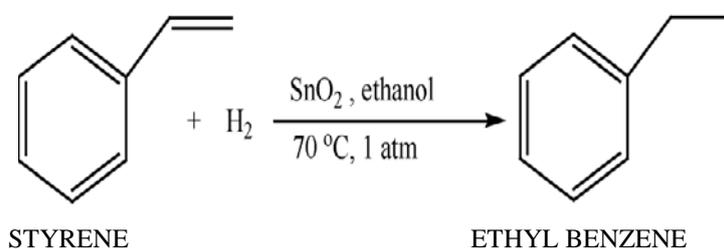
Fig. – 6: TEM micrograph of SnO₂ at different of reaction temperature (a) 30⁰C (b) 50⁰C (c) 70⁰C (d) 90⁰C. [Scale bar: 50 nm]

Table-8: Particle sizes and surface area of SnO₂ prepared at different reaction temperatures. Ammonia concentration: 3.20 M and ammonia feed rate: 0.1 mL min⁻¹.

Sample	Temperature (°C)	Particle size(nm)		Surface area(m ² g ⁻¹)
		TEM	XRD	
BT1	30	4.8±1.3	5.9	79
BT2	50	4.5±1.2	5.6	83
BT3	70	4.4±1.2	5.1	92
BT4	90	4.1±1.04.8		94

It was found that the surface area decreases with increasing ammonia concentration due to particles agglomeration. The slower ammonia feed rate produced a significant effect on particles size and distribution. A very slow feed rate led to bigger particles. Higher reaction temperature results in smaller particle sizes and larger surface area.

The catalytic activities of tin oxide nanoparticles prepared were investigated in the hydrogenation reaction of styrene. It was revealed that tin oxide prepared in high alkaline condition (pH 10.2) exhibited high catalytic activity with the percentage of conversion around 72%. Meanwhile, higher reaction temperature during the preparation of tin oxide also resulted in higher product conversion.



2) Carbon-based sulfonated catalyst (CBSC) becomes a research hot-spot in recent Years. In the preparation of CBSC, various carbon raw materials, various sulfonating agents, and various carbonization operation conditions have been developed. Biomass derived CBSC would be promising as biomass is renewable, abundant, low-cost, and easy for preparation. CBSC was widely studied and showed high catalytic activities in many chemical reactions, including hydrolysis, dehydration, esterification, alkylation, condensation, oxathioketalization, dimerization, benzylation and trimethylsilylation, etc. CBSC is a high potential solid acid catalyst due to its high catalytic activities and extensive applications.²³

iii) Energy Storage

a) Carbon Black

Carbon black is a material produced by incomplete combustion of heavy petroleum products. Various applications of carbon black in electronics have been found, one such is described²¹. A unique carbon black having high surface area and simultaneously low structure are desirable for use in energy storage application. The carbon black product having nitrogen BET surface area of about 600 m²/g to about 2100 m²/g was found. Thus it provides the potential benefit for energy storage application²⁴.

b) Graphene

Graphene is a substance composed of pure carbon. It is an allotrope of carbon whose structure is single planar sheet. The Nobel Prize in physics for 2010 was awarded to Andre Geim and Konstantin Novoselov at the University of Manchester for groundbreaking experiments regarding the two dimensional material graphene.²⁵ The specific surface area for graphene composite material of about 800 m²/g, 1200 m²/g and 1800 m²/g was observed. Thus it helps for energy storage²⁶.

c) Graphene/polyaniline (PANI) nanocomposites were prepared by reducing graphene oxide with hydrazine in the presence of different amounts of polyaniline nanoparticles. Transmission electron microscope (TEM) images of a graphene oxide (GO)/PANI solution revealed that the PANI nanoparticles were anchored on the surface of the GO sheets. During the reduction, the as-adsorbed PANI nanoparticles were sandwiched between layers of graphene sheets. These PANI nanoparticles acted as spacers to create gaps between neighboring graphene sheets, resulting in a higher surface area compared to pure graphene. Graphene/PANI nanocomposites exhibited the high specific surface area of 891 m²/g with supercapacitor properties.

CONCLUSION

Surface area has found to be an essential tool and its various aspects have been reported. A plethora of methods are available for the calculation of surface area and can be easily studied. For pharmaceutical industry, FDA Guidelines mentions along with particle size surface area of new drugs for new drug application needs to be mentioned for drug substances, as it directly affects the bioavailability and stability of final dosage form²⁸. Surface area proves to be an exploratory tool for the studies related to excipient, nanoparticles, mesoporous materials, drug delivery systems especially to develop pulmonary delivery system. The surface area of material also plays an important role such as it can be used in cement industries, adhesives, electronics, catalyst, hydrogen storage for fuel, energy storage and as supercapacitors.

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