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Extraction, characterization and co_2 adsorption studies of Silica from rice husk

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Abstract

Silica was isolated by pyrolysis and chemical treatment with NaOH from rice husk. Thus obtained silica was calcinated at different temperatures under different atmospheres. Highest surface area was recorded for the sample calcinated at 600°C under nitrogen atmosphere. This sample was labelled as $RHSiO_2$. To increase basic sites on $RHSiO_2$, amine impregnation was done by using MEA, DEA and PEI. On all these samples characterization studies like surface area, Pore size distribution, XRD, FT-IR, SEM were carried out. Infrared spectra of the silica is recorded by FT-IR spectrometer and the major chemical groups of silica are identified. The textural features of the amorphous silica observed by scanning electron microscopy (SEM) which clearly shows that amorphous silica has porous and multifaceted particle shape and size. CO_2 adsorption capacities are increased with increase in wt. % of amines like MEA, DEA and PEI. However 25 wt.% PEI shows more adsorption capacities at high pressures, as it contains more number of basic or nitrogen containing groups on the surface matrix.

Key words : Rice Husk, Silica, Amines, FT-IR, CO_2 adsorption

I. Introduction

Silica is the most abundant oxide in the earth's crust, yet despite this abundance, silica is predominantly made by synthetic means for its use in technological applications and it is one of the valuable inorganic multipurpose chemical compounds[1]. Although silica has a simple chemical formula (SiO_2), it can exist in a variety of forms, each with its own structural characteristics, as well as chemical and physical properties. Silica can exist in the form of gel, crystalline and amorphous material. Generally, the structure of SiO_2 is based upon a SiO_4 tetrahedron, where each silicon atom is bonded to four oxygen atoms and each oxygen atom is bound to two silicon atoms. The surface of silica consists of two types of functional group: silanol groups (Si-O-H) and siloxane groups (Si-O-Si). The silanol groups are the locus of activity for any process-taking place on the surface, while the siloxane sites are considered non-reactive[1]. Porous amorphous silica contains three types of silanol on its surface: isolated, geminal and vicinal[2].

The unequal distribution of the silanols in the matrix, resulting from irregular packing of the SiO_4 tetrahedral unit as well as the incomplete condensation, results in a heterogeneous surface (i.e., non-uniformity in the dispersion of silanol groups) for synthesized silica. The various silanols can have different adsorption activities and current knowledge indicates that the isolated silanols are the more reactive species. With increasing temperature of heat treatment, the silica surface becomes hydrophobic due to the condensation of surface hydroxyl groups resulting in the formation of siloxane bridges. Commercial silica manufacture is a multi-step process involving high heat and pressure, making it less cost effective and not very environmental friendly[3].

II. Literature Review :

Rice husk (RH) is an agricultural waste abundantly available in rice-producing countries. They are the natural sheaths that form on rice grains during their growth. These husk have no commercial interest as they are removed during refining of rice[4]. Increase of environmental awareness has led to a growing interest in researching ways of an effective utilization of rice by-product, from which rice husk is particularly valuable due to its high content of amorphous silica[5, 6]. The RH contains 80% organic volatile matters and remaining is silica. The chemical composition of the RH ash varies from sample to sample which may be due to the different geographical conditions, type of paddy, climatic conditions and type of fertilizer used[7,8]. It was found that RH char contains amorphous silica in addition to amorphous carbon as the main constituents[6]. Many authors have concluded that rice husk is an excellent source of high grade amorphous silica[9-12]. This portion of the silica cannot be dissolved in alkali and can withstand very high temperatures[13].

Active carbon has good adsorption property, can be produced from a variety of raw materials, such as packing papers, plastic bottles, by-products of the timber industry (e.g. sawdust), straw, rice husk, seeds or fruit shell can be mentioned. Interest is growing on agricultural waste for the production of activated carbon. Production of activated carbon from rice husk is achieved through activation with chemical or physical means[14,15]. Chemical impregnation with KOH, NaOH, $ZnCl_2$ or H_3PO_4 of pyrolysed rice husk followed by activation at 650–850°C results in activated carbons with extremely high surface areas (750–3014m^2/g)[16, 17]. The chemicals used to remove the silica so as to increase the pore in the rice husk. The RH ash is high in silica content and the loose wet structure of rice husk is destroyed after rice husk combustion in high temperature. While silicon dioxide is extracted from the RH ash, the carbon content is increased greatly in the residue, which is more economical for active carbon preparation in order to realize the farthest value of the agricultural waste. The objective of the research was to production of AC and amorphous silica from rice husk and characterize for efficient utilization of waste materials. The properties of amorphous silica and activated carbon from the available rice husks are comparable to some other studies[18,19].

III. Experimental procedure :

3.1 Preparation of raw materials :

Rice husk was collected from Krishna district, Andhra Pradesh, India and it was washed thoroughly with distilled water to remove adhering soil and impurities. Then it was dried in air at 110°C in an oven for 10 hours. The rice husk was milled and then passed through different sieves. The particle size between 40-50 mesh sizes was selected for further pretreatment.

3.2 Extraction of Silica from rice husk :

10 g of pyrolytic rice husk char was pretreated with 200 ml of HCl (1 M) to remove most of the impurities and to improve the purity of the silica. The char was introduced in a flask and the suspension was boiled for 3 hrs. under reflux condenser and vigorous stirring. Then, the suspension was filtered and the solid was washed with distilled water until the pH is neutral.

Finally the char recovered was dried for 15 hr. at 120°C. The next step was to extract silica with sodium hydroxide of different concentrations of 10, 15 and 20 wt. % solutions. The char and 200 ml of this solution was introduced in a flask and boiled for 4 hr. under reflux condenser. The suspension was filtered and the precipitate was washed with distilled water until the pH becomes neutral followed by drying at 120°C for 24 h. The precipitate is the resulting carbon material from which activated carbon materials can be prepared by chemical activation process. The filtrate is a solution of sodium silicate, which was subjected to a carbonation process in order to recover the silica. Thus, the solution was heated to around 80°C under continuous flow of carbon dioxide. After 1 h, the carbon dioxide flow was stopped and the solution was cooled down. Finally, the silica precipitate was filtered and dried at 120°C for 24 h and labelled as $RHSiO_2$. Thus obtained silica is calcinated at 400, 600 and 800°C respectively for 4 hr.[20, 21].

3.3 Catalyst preparation :

3.3.1 Preparation of Adsorbents

Amine incorporation on $RHSiO_2$

Amine incorporated silica was prepared by wet impregnation method. Briefly, desired quantity of MEA was dissolved in anhydrous methanol then silica prepared at different temperatures under N_2 atmosphere was added with vigorous stirring for 30 min. followed by drying at room temperature in nitrogen protection and vacuum drying at 110°C for 12 h [22]. A series of catalysts with 5, 10, 15, 20, 25 and 30 wt. % loadings of MEA were prepared. In similar procedure DEA and PEI were also impregnated on $RHSiO_2$.

3.4 Characterization and activity studies :

Pure $RHSiO_2$ and amine modified silica samples prepared in N_2 atmospheres at different temperature conditions were characterized for BET Surface area, Pore volume and FTIR techniques. However based on the textural properties like surface area and pore volume silica sample calcined at 600°C is used as support material for all catalyst preparations. The activities for these samples are evaluated by using a metal reactor interlaced with a gas chromatograph (Nukon-GC) at 40ml/min. flow rate at different temperatures 50°C, 70°C and 90°C. Different temperatures were implied to study the effect of temperature on CO_2 adsorption capacity. Carbon dioxide adsorption experiment was carried out on a lab made apparatus. 1 gram of the sample was loaded in metal reactor between the two quartz plugs and pretreated at 473K for 1 hr. in downstream of nitrogen at a flow rate of 40 ml/min. followed by cooling to desired adsorption temperature. Then a mixture of 10% CO_2 balanced helium was passed at a flow rate of 40 ml/min. until the adsorbent was saturated. The gas flows were controlled by mass flow controllers and temperature was controlled by PID controllers. The effluent gases were analyzed by gas chromatography (GC, Nucon Technologies, India) equipped with a thermal conductivity detector and having poropack Q column (3 meters length and 3 mm ID). The adsorption capacity was calculated from the break through curve (BTC).

IV. Results and Discussion

4.1 Proximate and ultimate analysis :

Proximate and ultimate analysis results of rice husk sample have shown in Table.1. The ash and fixed carbon of the analyzed char is in favor of Activated Carbon and Amorphous Silica production. The content of each of them depends on rice variety, soil chemistry, climatic conditions, and even the geographic location of the culture. In rice husk the fixed carbon varies from 12 to 18 and ash content varies from 17 to 22 [23].

Table 1. Proximate and ultimate analysis of rice husk

Proximate(wt.%)		Ultimate (wt,%, dry and ash free)	
Moisture	11.8	Carbon	37.3
Volatile matter	50.6	Nitrogen	0.7
Fixed carbon	15.3	Hydrogen	3.9
Ash	22.6	Oxygen	32.5
		Sulphur	0.1

Table 2. Surface are and Pore diameter of $RHSiO_2$ and amine impregnated catalysts

Sample	MEA		DEA		PEI	
	S.A(m^2g^-)	P.D.(n.m.)	S.A(m^2g^-)	P.D.(n.m.)	S.A(m^2g^-)	P.D.(n.m.)
Pure $RHSiO_2$	595.2	3.12	595.2	3.12	595.2	3.12
$RHSiO_2$- 5	574.5	3.05	562.3	3.05	548.9	2.71
$RHSiO_2$-10	558.3	3.08	548.1	3.0	509.5	2.78
$RHSiO_2$-15	512.1	3.0	512.6	2.86	486.5	2.54
$RHSiO_2$-20	484.7	2.96	483.7	2.89	461.7	2.41
$RHSiO_2$-25	412.6	2.98	446.0	2.78	432.8	2.64
$RHSiO_2$-30	395.2	2.98	423.5.0	2.70	418.8	2.58

4.2 Surface area and Pore volume :

Surface area and pore diameter of the adsorbents are shown in Table-2. The surface area of pure $RHSiO_2$ prepared in nitrogen atmosphere at 600°C is maximum when compared with other samples. The surface area, average pore diameters of MEA, DEA and PEI loaded with different wt. percentages are measured and listed in Table-2. The actual surface area of pure $RHSiO_2$ is 595.2 m^2g^- and the average pore diameter is 3.12 nm. After loading different wt. percentages of amines, in all these samples there is notable decrease in surface area and marginal decrease in pore volume is observed which might be due to blockage of the micro pores present on the texture of the support. These results suggests that the amount of amines on the silica does not affect much of the surface properties

4.3 XRD:

The X-ray spectra and characteristic absorption peak of silica have been obtained and shown in Fig.1, no pre-treatment has been performed on the sample. The sample is completely amorphous as indicated by the featureless diffractograms and the appearance of a diffuse maximum at 2ø of 22.5° typical for amorphous silica. The result confirmed the absence of any ordered crystalline structure.

4.4 Effect of NaOH and pyrolysis temperature on silica yield :

Silica yield increased with the increasing concentration of NaOH and also with the increasing temperature of pyrolysis. Fig.2 shows the effect of

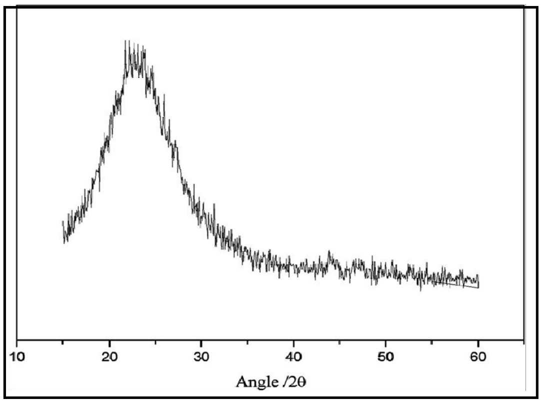

Fig.1 X-Ray diffraction of $RHSiO_2$

$$SiO2 + 2\ NaOH \rightarrow Na2SiO3 + H2O$$
$$Na2SiO3 + 2HCl \rightarrow 2NaCl + SiO2 + H2O$$

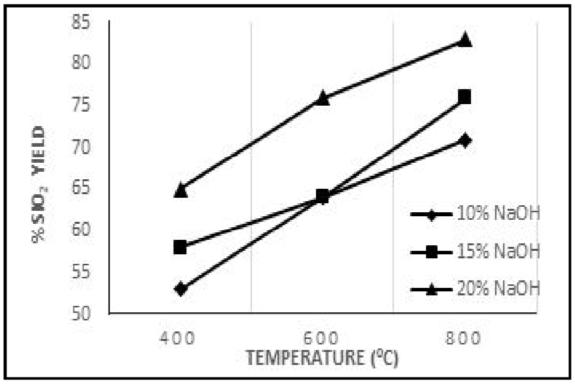

Fig. 2. Effect of NaOH and pyrolysis temperature on silica yield

NaOH and pyrolysis temperature on silica yield. Because Si–O parts were liberated from the long polymeric chains (Si–O–C / Si–O–Si) with temperature. As a result the yield of silica may increase due to liberated Si–O bonds. This SiO_2 is removed by alkali extraction

4.5 Functional Group Analysis of Silica :

Infrared spectra of the silica is recorded by FT-IR spectrometer and presented in Fig. 3, and the major chemical groups of silica are identified. The predominant absorbance peaks of silica are displayed in the low frequency region bands at 1200-1000 cm^{-1}, 807 cm^{-1} and 475 cm^{-1} due to asymmetric stretching, symmetric stretching and bending modes of bulk Si-O-Si. The band located at 3366 cm^{-1} and 955 cm^{-1} was ascribed to the SiO-H asymmetry stretching vibration and bending vibration. The band at 1670 cm^{-1} belonged to H-O-H bending vibration.

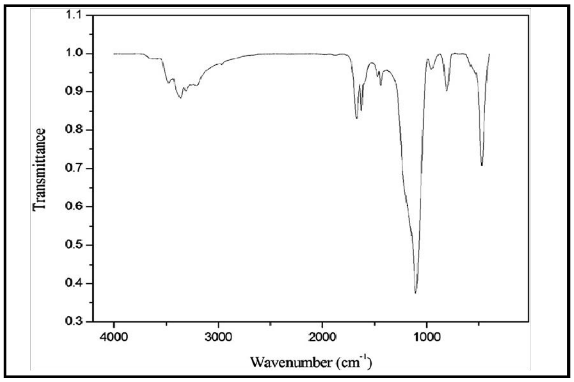

Fig. 3 FTIR spectra of Rice Husk extracted Silica

4.6 Surface analysis of silica :

The textural features of the amorphous silica observed by scanning electron microscopy (SEM) are shown in Fig. 4. From these figures it is clearly seen that amorphous silica has porous and multifaceted particle shape and size. The morphology seen in figure can be attributed to the burning out of the organic component in the rice husk during combustion. The primary particles size showed a tendency to from bigger particles (aggregates). The hydrated silica subsequently polymerizes to form a skeletal silica network which may explain in the SEM micrograph in Fig. 4.

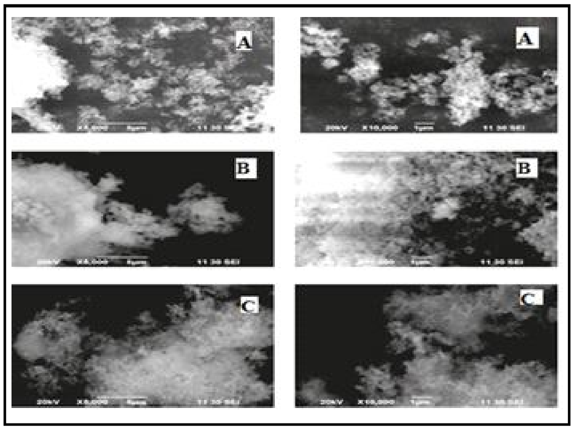

Fig. 4 SEM images of $RHSiO_2$ at different calcination temperatures
A) 400ºC B) 600ºC C) 800ºC

4.7 Effect of amine loading on CO_2 adsorption :

Generally in any catalysis reaction, surface area, pore volume and average pore diameter will play an important role in adsorption capacity of adsorbents. Isotherms of CO_2 on modified $RHSiO_2$ samples.at 50ºC and 1 atm pressure is depicted in Fig.5. It can be seen that the amounts of CO_2 adsorbed on all modified $RHSiO_2$ samples increase with increase in the amount of MEA, DEA and PEI from 5 to 25 wt.%. This trend is due to increase in basic sites or amine groups, in turn increases the CO_2 adsorption. This may also be attributed that up to 25 wt. % loading monolayer of amines might be formed and after that amine multilayer formation might have taken place, which reduces the exposure of more number of active sites like basic groups. This leads to decrease in adsorption capacity when the amount of amines is increased to 30 wt. % and higher. This may also be attributed to the pore filling effect that blocks the pores of adsorbent preventing CO_2 to diffuse in to the pores.

4.8 Effect of Pressure on CO_2 adsorption:

For pure $RHSiO_2$ sample the rate of adsorption is negligible when compared with 25 wt.% PEI modified silica. As pressure increases rate of adsorption remains almost constant in pure silica but increases gradually in case of PEI modified silica, shown in Fig. 6. The adsorption of CO_2 on pure $RHSiO_2$

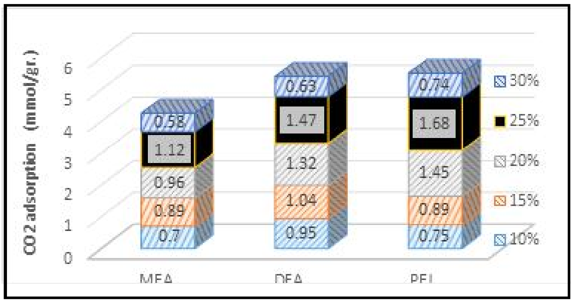

Fig. 5 CO_2 adsorption (BTC) on modified $RHSiO_2$ samples with MEA, DEA, PEI amine groups

sample is very poor, which may be attributed that the basic sites on pure sample are negligible and hence adsorption is very less. However, the CO_2 adsorption on pure sample may not be considered as physical adsorption, but may be some of CO_2 molecules are trapped in the micropores of silica. In case of PEI modified silica, the rate of adsorption increases with increase in pressure due to formation of multilayer of CO_2 on the surface of catalyst.

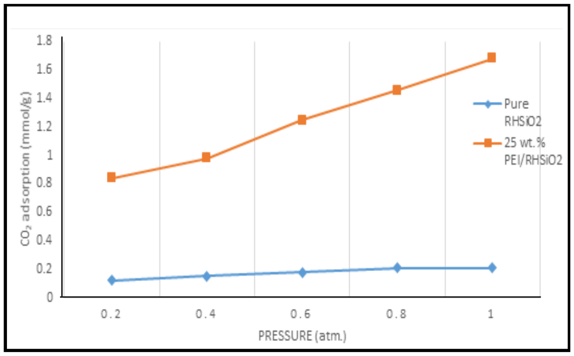

Fig. 6 Effect of Pressure on CO_2 adsorption at 50°C temperature

4.9 Effect of Temperature on carbon dioxide adsorption:

25 wt.% PEI loaded $RHSiO_2$ sample shows more CO_2 adsorption than MEA and DEA modified samples which is shown in Fig.7. As temperature increases the PEI modified $RHSiO_2$ shows higher CO_2 adsorption capacities than the other samples. The Fig.7 shows the isotherms of CO_2 of 25 wt. % PEI loaded on $RHSiO_2$ at 50, 70 & 90°C and 1 atm pressure.

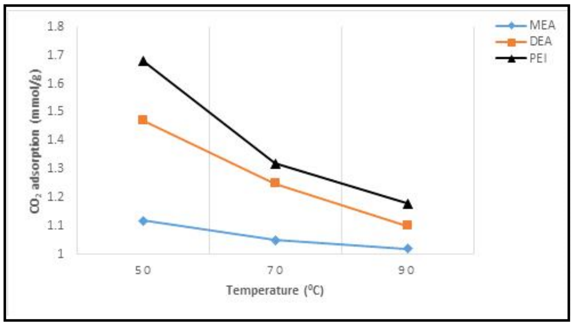

Fig. 7 Effect of Temperature on carbon dioxide adsorption

When the pressures are increased, the adsorption capacities of the $RHSiO_2$ modified with PEI up to 25 wt. % is significantly higher though the surface area and pore volume are lower than the pure $RHSiO_2$. It implies that chemical adsorption dominates the CO_2 adsorption on the modified $RHSiO_2$. The results confirm that the increase in the pressure facilitates the transfer of the adsorbed CO_2 molecules from the surface in to the bulk of PEI by overcoming physical adsorption. On the other hand, increase in temperature above 50°C reduces the carbon dioxide adsorption capacity, as the forces of attraction between adsorbent and adsorbate starts breaking at higher temperature. The adsorption capacities have same trend for all series of catalysts. The notable point is that the modified PEI 25 wt. % samples at 50°C has higher CO_2 adsorption capacity than that at 70 and 90°C.

V. Conclusion

Silica was successfully isolated from rice husk by using NaOH as reagent. As percentage of NaOH increases the percentage of silica extracted was also increased. The amine modified $RHSiO_2$ have been synthesized in laboratory for carbon dioxide adsorption studies. CO_2 adsorption capacities are increased with increase in wt. % of amines like MEA, DEA and PEI. However PEI shows more adsorption capacities at high pressures, as it contains more number of basic or nitrogen containing groups on the surface matrix. Adsorption capacity on all the samples gradually increases from 5 wt. % to 25 wt. % of amines and then shows decreasing trend. This may be due to amine multilayer formation and pore blocking. At low temperature around 50°C amine modified $RHSiO_2$ shows more adsorption than at high temperatures. From this it can be concluded that the adsorption capacities of PEI modified samples can be enhanced at optimum temperatures. However, this has to be optimized under different atmospheres and calcination conditions. The isolated silica from rice husk can also be used as support for different catalysts for dehydration of alcohols, dehydrogenation etc. reactions, which is our future plan of action.

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