Evaluation of Synthetic Conditions for H_3PO_4 Chemically Activated Rice Husk and Preparation of Honeycomb Monoliths

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Abstract

Activated carbons in this work were prepared from rice husk by phosphoric acid activation followed by alkaline desilication. Pseudo-random selection of 16 rice husk samples was subjected to carbonization at the following conditions: 0.5 to 2 h of activation time, 300-600 ºC and H_3PO_4/precursor (wt/wt) impregnation ratio of 0.5 to 2. Concentration of NaOH desilication solution varied from 0.5 to 2M. It was found that out of the four factors impregnation ratio is clearly the strongest and at the impregnation ratio of 2 for 1 h at 500 °C N_2 BET-surface area reaches 1690 m^2/g ($S_{BET\,(Ar)}$=2492 m^2/g) while pore volume becomes 1.95 cm^3/g. Elemental analysis showed highest carbon content for this sample (87.96%). All samples have insignificant amount of Si and traces of metals, but considerable amount of phosphorus. Blocks of honeycomb structure prepared from Ca-montmorillonite and desilicated carbonized rice husk (impregnation ratio is 1.5, 1 h at 600 ºC) have BET-surface area obtained by thermal desorption of argon up to 856 m^2/g.

Introduction

Rice husk, a by-product of rice milling industry, is a waste with the annual world production of ca. 545 million tons [1]. In the rice producing countries, rice husk is used as a fuel. However, this product is characterized by low caloric value, 13–15 MJ/kg [2], and high mineral content. On the other hand, rice husk as a lignocellulose biomass is a valuable carbonaceous precursor that can be used to obtain a carbon material with special textural properties, high specific surface area and large pore volume [3].

The manufacture processes of activated carbons include physical or chemical methods. Both methods have previously been investigated to produce activated carbons from rice husk. Activated carbons with surface area of 273 m^2/g were produced from rice husk by one-step steam activation [4]; activated carbons with surface areas as high as 3000 and 2500 m^2/g were prepared from rice husk by KOH and NaOH chemical activation [5, 6]. Activated carbons with surface areas of 1100 m^2/g in pores greater than 1 nm was prepared from rice husk by $ZnCl_2$ activation [7]. Activated carbons prepared from rice husk by H_3PO_4 activation have been investigated for the removal of different pollutants [8, 9], however, limited information about the properties of these carbons was provided. Highly mesoporous carbons with relatively low surface area and total pore volume were obtained from rice husk through a two-stage process (precarbonization followed by H_3PO_4 activation in temperature range of 700–900 °C) [10]. Activated carbon with BET surface area and total pore volume as high as 874 m^2/g and 0.713 cm^3/g was also prepared from rice husk by H_3PO_4 activation [11].Previous results indicated that activated carbons with desirable surface area and pore structure can be prepared from rice husk. However, high mineral content of activated carbons prepared from rice husk by H_3PO_4 activation, which is usually in the range of 20–70% [8, 9,11], prohibits their application and commercial production. In view of that phosphoric acid-activated carbons have been proven to be highly effective adsorbents for the removal of heavy metal ions from aqueous solutions [12] because of their remarkable high cation-exchange capacities, which is due to the existence of a large number of acidic surface groups that provide exchangeable protons [13]. Considering its plentiful and renewable supply, rice husk as a starting material for the production of activated carbon by H_3PO_4 activation deserves more intensive investigation [14].

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Printed in Kazakhstan

In a multitude of previous studies on H_3PO_4 chemical activation of lignocellulosic materials it has been suggested that the optimal conditions to attain highest surface area are 0.5 to 2 h of activation time, 450-550 ºC and H_3PO_4/precursor (wt/wt) impregnation ratio of about 1.5 up to 2. To elucidate the trends of how these parameters affect the yield, specific surface area and development of pore structure of carbonized rice husk (CRH), reasonably broader ranges were chosen and concentration of leaching solution to remove most of minerals was added as a variable. To achieve this objective, a two-step H_3PO_4 activation-desilication process (acid/base treatment) was applied to a pseudo-random selection of rice husk samples (just 16 combinations to minimize the experiment).

When choosing adsorbents and catalyst supports, highly developed porous structure is a preferable property. A special niche in this field belongs to natural porous materials [15, 16] including rice husk [17, 18]. Usually, these materials are represented by powders or granule pieces having wide particle size dispersion and low mechanical strength. One of the promising directions of their practical application is extrusion as monoliths with a regular honeycomb structure.

The goal of this work is also to prepare honeycomb monoliths from carbonized rice husk with the emphasis on control of textural characteristics and extension of functional properties on the basis of well known methods [19] and our previous experience [20, 21].

For direct extrusion of carbon monoliths, a large amount of binder should be added because of low plasticity of carbon materials. Natural clays, in particular montmorillonite $Ca_{0.2}(Al,Mg)_2Si_4O_{10}(OH)_2{\bullet}4H_2O$ (Ca-M), are commonly used as a binder [20,21, 22]. On the one hand, binder increases the plasticity of carbonaceous molding composition and mechanical properties of monoliths. On the other hand, the increased mechanical strength of products has negative effect on their porous structure since a part of pores is plugged with a binder. To enhance the porosity of composite monolith substrate the chemical treatment of finished monoliths or their initial components with KOH and Na_2CO_3 solutions can be applied. This technique of alkaline treatment early was used for carbonized rice husk and a considerable development of the porous structure achieved [5, 6, 23, 24].

Experimental

Synthesis of carbonized rice husk materials via H_3PO_4 activation followed by desilication

Precarbonization

16 glass jars having 30 grams of rice husk each and the appropriate amount of admixed 70% phosphoric acid ($\rho \approx 1.53$ g/cm^3) were placed into an oven and heated at 200 ºC overnight. Precarbonized contents of the jars were transferred into quarts test tubes and loosely covered with stoppers (4 series of 4 test tubes).

H_3PO_4 Chemical activation

A series of 4 test tubes with the material impregnated at different ratios was placed into a vertical cylindrical furnace equipped with chromel/alumel thermocouple. Each time a series was heated at the rate of about 5 ºC /min to a desired temperature and the temperature was maintained for 2 hours. Every half hour a test tube was quickly removed from the furnace, cooled to room temperature, cautiously half filled with distilled water then cooled again. Carbonization was conducted under access of air.

Neutralization

The carbonized materials was removed from the test tubes and neutralized to Na_2HPO_4 with the equivalent amount of concentrated NaOH solution in Pyrex glass beakers and refluxed for 10 min. Solution was decanted upon sedimentation and washed twice with about the same amount of hot distiller water to lower the buffering power of residual Na_2HPO_4 solution.

Desilication

The residue upon decantation was filled with 2 liters of NaOH solution of appropriate concentration (0.5 to 2 M) in the same vessel and boiled for 30 minutes to remove SiO_2, then let stay to sediment. The solution was decanted to remove sodium silicate.

Washing and drying

It took 5-7 times of standard procedure of washing with 5 l of distilled water (through boilingsedimentation-decantation) for about 10 grams of residual carbon materials to reach the equilibrium of pH~7. The samples were dried in hot air oven for at least 12 h at 110±5 °C, weighted, sealed in airtight containers and appropriately labeled.

Monoliths preparation

To make monoliths we used Ca-montmorillonite together with desilicated CRH obtained under following conditions: impregnation ratio is 1.5, carbonization for 1 h at 600 ºC, neutralization with NaOH to Na_2HPO_4 and desilication by 3 h reflux of 75 g of product material in 1.5 l of 12% KOH followed by washing with distilled water and drying ($S_{BET\ (Ar)}$ =1755 m^2/g). Final product, labeled as CRH_SiO_2-P-500_desil, was grinded into powder with particle size of ca. 50-100 μm. Ca-M was dispersed in water under intense stirring with electric stirrer to obtain a homogeneous suspension. The suspension was poured into a flat vessel and allowed to stay open for several days until the clay swelled and a viscous mass with the moisture content 65-68% formed. The CRH_SiO_2-P-500_desil powder and Ca-M suspension were blended in a Z-shape mixer for 15-30 min. The optimal weight ratio of CRH to Ca-M necessary to obtain a plastic mass is 1: 1 in terms of the calcined substance. Moisture content of the mass ready for molding is 55–60%. First the mass was consolidated and compacted by vacuum, then extruded through a die plate 10 mm in diameter using a pneumatic press with vertical piston. This was followed by drying, which is an essential preparation step. Moisture transfer and shrinkage proceeding in a wet monolith have impact on the finished product shaping (bending, channels rupture, cracking) and mechanical strength. Thus, the formed monoliths were first seasoned for 3 days in cartons permeable to water vapor, then dried at 100 °C, and calcined at 700 °C in flow of Ar for 4h. The chosen calcination temperature provides high water resistance of monoliths.

Physical methods of investigation

Investigation of the specific surface area by BET method

Thermal desorption of argon

Specific surface area ($S_{BET(Ar)}$, m^2/g) of the samples were determined by argon thermal desorption (BET method) using analyzer SORBI N.4.1., comparing the amount of adsorbate gas (argon) adsorbed by a sample with the standard sample of known surface area. Mixture of argon with a carrier gas (helium) was passed through the adsorber with the test sample at the temperature of liquid nitrogen until the establishment of adsorption equilibrium. The sample is then heated to a complete desorption of argon from the sample surface. Change of argon concentration in the flow of gas mixture during the adsorption and desorption is recorded. On the resulting graph desorption peak areas are proportional to the volume of desorbed gas. The values of the specific surface area were calculated by use of BET theory (Brunauer, Emmett, Teller).

Low-temperature nitrogen adsorption

Information on microporous & mesoporous texture (range from 17 to 3000 Å) of some carbonized RH sample was obtained by the method of low-temperature nitrogen adsorption using “ASAP-2400” Analyzer (Micromeritics Instrument Corp.,Norcross, GA, USA), upon preliminary training of the samples at 150°C & residual pressure lesser than 0.001mmHg. Then the measurements of nitrogen adsorption isotherms were conducted at the temperature of liquid nitrogen (77 °K) within range of relative pressures from 0.005 to 0.991.

Elemental analysis

Qualitative analyses of mineral part of the sample were performed using X-ray fluorescent spectroscopy on VRA-30 analyzer with Cr-anode X-ray tube; as well as using energy-dispersion analyzer “SPRUT-001”.

Carbon, hydrogen, nitrogen and sulphur contents were determined by use of elemental analyzer “VARIO ELEMENTAR III”.

Scanning electron microscopy

The morphology of CRH and monoliths was studied by scanning electron microscopy (SEM) using a JSM 6460LV microscope (JEOL, Japan) with accelerating voltage of 25 kV.

Results and Discussion

Phosphoric acid is a known porogen letting the carbonization reactions to occur at substantially lower temperatures (probably due to acidic catalysis and dehydration) compared to standard pyrolysis which governed mostly by radical processes leading in turn to disproportionation reactions yielding tar formation. The use of phosphoric acid is therefore to provide both carbon retention (higher yields, *e.g.*: less amount of volatiles are formed as hydrocarbon tar) and high surface area (no tar- no need in gasification).

In our previous experience with H_3PO_4 activated CRH we found that it takes unreasonably long time to get rid of H_3PO_4 by simple washing with distilled water: SiO_2 species formed in presence of H_3PO_4 at high temperatures (600 °C) continuously washed out from carbon matrix in colloidal form. Knowing that Na_2HPO_4 is about neutral, to facilitate and expedite the process, we used neutralization procedure according to the equation:

$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O \qquad (1)$$

In the case of silicon containing carbon composites the use of alkaline agents such as NaOH or KOH is an extra way to obtain mesoporous materials due to washing out from the matrix the water-soluble Na or K silicates forming by the reaction:

$$2MeOH + SiO_2 \rightarrow Me_2SiO_3 + H_2O \qquad (2)$$

where (Me = Na, K), and SiO_2 serves as a template for pore formation. So we used various concentrations of NaOH solution to find out how the degree of SiO_2 leaching affects the surface area (see Table1).

For the samples with highest surface area in each series, to further study their textural properties, low-temperature nitrogen adsorption method was used (see the results in Table 2. Pore size distribution is depicted on Fig.1 and 2.) The standard calculations for isotherms were performed by Barret-Joyner-Halenda method, with the admission of postulated model for cylindrical pores, the calculation of total pore surface area S_Σ and micropore surface area S_μ by BET-method, total pore volume V_Σ and micropore volume V_μ; average pore diameter $D_{pore\ average}$ (inclusive of micro- and mesopores). The method capability regarding pore size distribution is restricted only for the mesopores range. According to these results, the largest portion of pores is accounted for mesopores, these pores volume and surface area may be calculated by subtraction of the values of micropore volume and surface area from corresponding total values (Table 2). At the same time substantial amount of micropores are present in the samples #4 and #13. Mesopore size is mainly about 4 nm and the pore size ranges from 3 to 40 nm (Fig.2).

Elemental content of the samples ## 4,6,11 and 13 show traces of metals and other elements, a lot of phosphorus, especially for #13 (probably due to covalent C-O-P bonding), but almost no silicon (which signifies successful desilication, see Table 3).

Highest carbon content for samples #6 and #11 compared to #13 and #4 (Table 4.) indicates higher degree of carbonization and correlates with high surface area and pore volume.(Table 2)

For monoliths preparation, considering the effect of CRH_SiO_2-P-500_desil to binder (Ca-M) ratio on plasticity of the molding material, its composition was optimized and contains 50% of CRH and 50% of Ca-M in terms of the calcined substance. Our

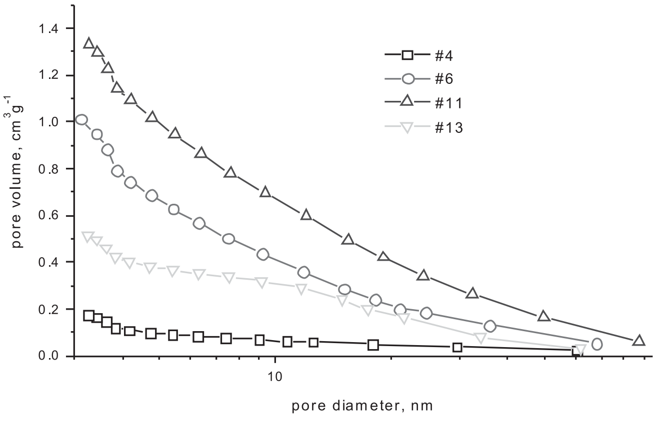

Fig.1 Integral pore size distribution in CRH samples ## 4,6,11,13

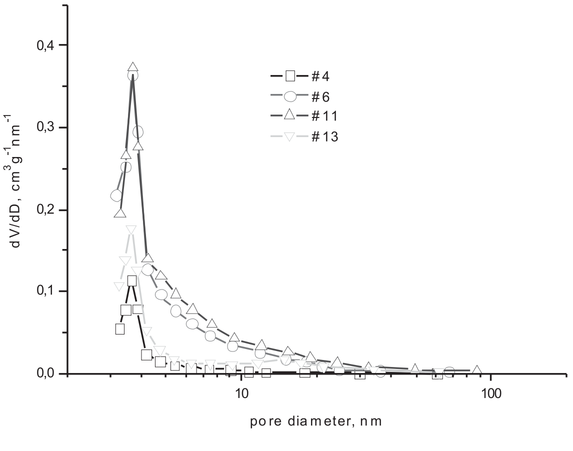

Fig.2. Differential pore size distribution in CRH samples ## 4,6,11,13.

Table 1.

Argon thermal desorption BET surface area and yield of carbon as functions of the parameters

Sample number (#)	T, ºC	Impregnation ratio by weight H_3PO_4/ RH	Carbonization duration, h	C_{NaOH}, M	$S_{BET (Ar)}$, m^2/g	Carbon weight, g	Yield, %
1	300	0.5	0.5	2	206	12.66	42.2
2	300	1	1.5	1.5	428	11.69	38.97
3	300	1.5	1	1	769	9.74	32.5
4	300	2	2	0.5	1147	8.01	26.7
5	400	1.5	0.5	1	1600	9.17	30.57
6	400	2	1.5	0.5	2300	7.84	26.13
7	400	0.5	1	2	551	9.85	32.83
8	400	1	2	1.5	1759	9.67	32.23
9	500	1	0.5	0.5	1070	9.63	32.1
10	500	1.5	1.5	2	1730	9.02	30.07
11	500	2	1	1.5	2492	7.99	26.63
12	500	0.5	2	1	667	9.76	32.53
13	600	2	0.5	1.5	2010	9.95	33.17
14	600	0.5	1.5	1	866	10.59	35.3
15	600	1	1	0.5	1671	12.04	40.13
16	600	1.5	2	2	2147	9.32	31.07

The table1 results suggest that:

1 Concentration of alkali was too high to see the expected effect on the surface area by partial leaching (e.g. even 0.5 M NaOH is strong enough to dissolve SiO2 species in carbonized moiety in proportions of 2 liters of solution per about ten grams of the final products (see elemental analysis in Table 3 for the samples 4 and 6)

2. Out of the four influencing factors impregnation ratio is clearly the strongest and at the impregnation ratio of 2 the specific surface area is the highest while at 0.5 is the lowest in each series of the samples (## 4,6 11,13 and 1,7 12,14 respectively).

3. Time and temperature seem to be less critical in general at the chosen scale, however for the sample #4 at 300 ºC even 2 h is not enough to reach the value of the surface area of sample #5 (1147 m2/g vs. 1600 m2/g) heated at 400 ºC for only half hour even though impregnated at lesser value (1.5 vs. 2). On the other hand when it comes to sample #13 in comparison with #6 (400 ºC, 1.5 h, both impregnated at the same ratio of 2), 0.5 h at 600 ºC is seemingly not enough to undergo sufficient carbonization.

4. In general, there is a good correlation between the surface area and yield of carbon material: the lesser is yield- the higher is surface area. The relatively smaller yields of the samples with the ratio of 0.5 at higher temperatures could be explained by competition of physical with chemical activation processes.

Table 2.

Textural properties of CRH-samples obtained from nitrogen adsorption (BET) method

Sample number (#)	S_Σ	S_μ, m^2/g	V_Σ, cm^3/g	V_μ, cm^3/g	$D_{pore\ average}$, nm
4	964	420	0.6	0.2	1.8
6	1476	0	1.5	0	4.0
11	1690	0	1.95	0	4.4
13	1552	196	1.17	0.094	3.0

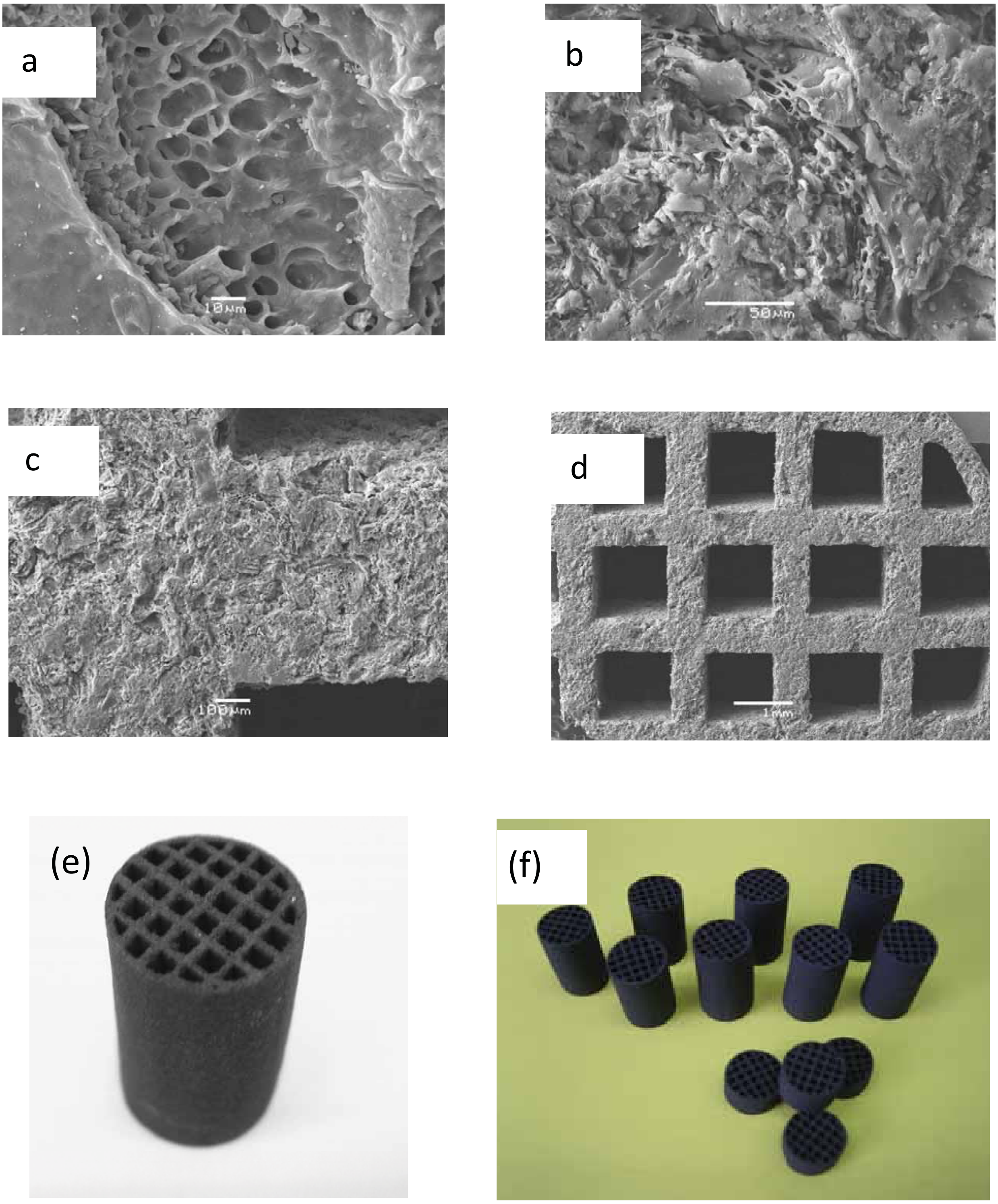

Fig. 2. SEM images of the CRH and honeycomb monoliths: a – CRH_SiO_2-P-500; b – a piece of CRH_SiO_2-P-500_desil imbedded into Ca-montmorillonite within the block structure; c, d – SEM images of monolith partitions; e, f – external appearance of the monoliths

Table 3.

Inorganic Elemental composition of some CRH samples (%)

#/element,%	Al	As	C,H,N,O	Ca	Cl	Cr	Cu	Fe	K	Mg	Mn	Ni	P	S	Si	Ti	Zr
4	0	0	99.1455	0.0143	0.0032	0	0	0.0032	0	0	0	0.0011	0.767	0.024	0.0266	0	0.0003
6	0.0084	0.0032	99.4873	0.0209	0	0.0013	0	0.0062	0.0005	0	0.0004	0	0.4102	0.0141	0.0338	0	0
11	0.0038	0.0026	98.999	0.0188	0	0	0.0008	0.0018	0.0056	0	0	0	0.8947	0.0147	0.0375	0	0
13	0.0063	0.0038	97.29	0.1572	0	0	0.001	0.0066	0.0038	0.0024	0.0047	0.0009	2.4422	0.0094	0.0876	0.0014	0

Table 4.

C,H,N,O,S-content of the samples

#	C, %	H, %	N, %	O^a, %	S, %
4	72.88	2.95	0.3	22.82	0.19
6	87.88	2.42	0.2	8.8	0.18
11	87.96	1.92	0.26	8.62	0.23
13	78.33	1.92	0.51	16.37	0.15

[a] Oxygen was calculated by difference inclusive of mineral part.

previous experience showed that Ca-M provides good plasticity of the molding composition due to its ability to swell in the presence of water that penetrates into the interlayer space of this clay. On the other hand, Ca-M as a monolith component retains its ability to absorb water, whereas the monoliths should have high water resistance for their further application as catalyst supports or adsorbents. So the monoliths with montmorillonite clays were calcined at 700 °C, the temperature that provides irreversible joining of the interlayer space, which makes it possible to obtain products with high mechanical strength and water resistance. Upon silica leaching (single treatment with 12% KOH followed by water washing) the BET-surface area (thermal desorption of argon) of the blocks became 856 m^2/g

Fig. 2 shows a general view of CRH monoliths (e, f). SEM images of cross-sections of monolith (Fig. 2c and 2d) and monolith material at high magnification (Fig. 2a and 2b) demonstrate that morphological properties of the material are determined by the morphology of monolith components, fragments of CRH and Ca-M.

Conclusion

Analysis of two-step H_3PO_4 activation-desilication process applied to a random selection of 16 rice husk samples showed that the N_2 BET-surface area as high as 1690 m^2/g ($S_{BET\ (Ar)}$=2492 m^2/g) and pore volume of 1.95 cm^3/g was achieved with sample obtained at the following conditions: 500 °C, impregnation ratio of 2, and 1 hour of carbonization. The yield of this product on a larger scale reached 30%.

Honeycomb Monoliths were prepared from mixture of Ca-montmorillonite and the sample CRH_SiO$_2$-P-500_desil. BET-surface area (thermal desorption of argon) of the material of obtained blocks equals to 856 m^2/g. These materials could be used as catalysts or adsorbents.

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Received 25 february 2009.