Catalysis Today 147S (2009) S58–S65

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Preparation of carbonized rice husk monoliths and modification of the porous structure by SiO_2 leaching

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ARTICLE INFO

Article history:
Available online 5 August 2009

Keywords:
Honeycomb monoliths
Rice husk
Carbonization
Textural properties
Silica leaching

ABSTRACT

The possibility of preparing honeycomb monoliths from unconventional materials with high adsorption capacity, such as carbonized rice husk (CRH), was studied. Two schemes including modification of the porous structure by silica leaching were suggested for preparation of the monoliths: (1) preparation of CRH monoliths with the addition of Ca-montmorillonite (Ca-M) followed by leaching and (2) preliminary leaching of initial components followed by monolith extrusion. Chemical and textural properties of the materials were studied at each preparation step. The effect of temperature of rice husk (RH) pyrolysis and conditions of leaching treatment on the physico-chemical properties of CRH was investigated. By the data of nitrogen adsorption and SEM characterization, CRH has low specific surface area, pore volume less than 0.1 cm^3/g, and composed mainly of macropore channels 5–10 μm in diameter, micropores less than 17 Å in size, and a minor amount of mesopores. Treatment of the carbonized product with a 12% solution of potassium hydroxide at 80–100 °C leads to a 90–95% leaching of SiO_2 from the CRH composite and increases the specific surface area to 400 m^2/g and pore volume to 0.4 cm^3/g due to formation of mesoporous structure. The feasibility of CRH honeycomb monoliths preparation and applicability of silica leaching from the monolith material for modification of the porous structure are demonstrated. The resulting monoliths are characterized by specific surface area exceeding 300 m^2/g, pore volume 0.3 cm^3/g, and high mechanical strength.

1. Introduction

Honeycomb monoliths have some advantages over granulated and powder materials. Low-pressure drop and large geometric surface area per unit volume make them attractive for catalysis. Chemical composition of the monoliths, morphology of their components, porous structure and geometrical parameters determine their properties, mechanical strength, surface area, resistance to the action of water and various chemical agents, which in turn determine the functional properties of the monoliths in adsorption and catalytic processes [1–3]. 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 [4–16] including rice husk [5,6,13,14].

Rice husk, a by-product of rice milling industry, is a waste with the annual world production of ca. 545 million tons [14]. 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 [17], and high ash 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 [18–21].

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.

There are several approaches for preparation of carbon containing composite monoliths [22], by carbonization of carbon precursors on the surface of cordierite monolithic substrate, c.a. sucrose [23] and polyfurfuryl alcohol [24], or by growing of carbon nanofibers in porous structure of a substrate [25,26]. 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 $Ca_{0.2}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}4H_2O$ (Ca-M), are commonly used as a binder [27–30]. On the one hand,

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doi:10.1016/j.cattod.2009.07.043

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 was achieved [18–21].

The alkaline treatment being applied for monolithic structure, will allow modifying the porous structure of monoliths due to formation of new pores upon removal of silica both from the carbon component of monolith and from montmorillonite that was used as a binder.

The goal of this work is to develop methods for honeycomb monoliths preparation from carbonized rice husk with the emphasis on control of textural characteristics and extension of functional properties on the basis of well-known methods [31,32] and our previous experience [27–30].

2. Experimental

2.1. Rice husk carbonization

The carbonization was carried out via RH pyrolysis in argon atmosphere at 400–800 °C for 60 min after attaining a desired temperature with a ramp rate 2.5 °C/min. For carbonization, 500 cm^3 of RH was placed in a steel reactor and heated in a muffle furnace.

2.2. Monoliths preparation

For monoliths preparation we used rice husk carbonized at 700 °C and Ca-montmorillonite. The CRH, initial or after the alkaline treatment, 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 powder and Ca-M suspension were blended in a Z-shape mixer for 15–30 min. The optimal content of CRH to Ca-M necessary to obtain a plastic mass is 60 and 40% respectively in terms of the calcined substance. Moisture content of the mass ready for molding is 45–50%. First the mass was consolidated and compacted by vacuum, then extruded through a die plate 10 mm in diameter using a pneumatic press with a 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 flowing Ar. The chosen calcination temperature provides the 100% water resistance of monoliths.

2.3. Chemical treatment with alkaline agents

The finished monoliths made of CRH were treated with a 12% solution of KOH or Na_2CO_3 at 80–100 °C for 3 h. The volume ratio of liquid and solid was 10:1. After treatment in the KOH solution, samples were washed out repeatedly with a large amount of distilled water to remove soluble compounds of Si. Then the monoliths were blown by air to remove moisture from the channels and dried at 100 °C for 2 h. The steps of alkaline treatment and washing with water were repeated up to four times. The same KOH treatment procedure was used for initial CRH and Ca-M when monoliths were prepared by using preliminarily treated components.The monolith samples were treated also by impregnation with a saturated Na_2CO_3 solution followed by drying at 100 °C and calcination at 700 °C in Ar. Then the sample was washed repeatedly with distilled water and dried at 100 °C for 2 h. The steps of treatment with sodium carbonate and washing with water were repeated four times.

2.4. Physical methods of investigation

The textural properties of CRH samples, Ca-M and monoliths were studied by low-temperature nitrogen adsorption with an ASAP-2400 analyzer (Micromeritics Instrument Corp., Norcross, GA, USA) after samples pretreatment at 150 °C. The nitrogen adsorption isotherms were determined at the liquid nitrogen temperature, 77 K, in the range of relative pressures from 0.005 to 0.991, which was followed by a standard processing by the Barret–Joyner–Halenda scheme to calculate the total surface area A_{BET}, total pore volume V_Σ and micropore volume V_μ. The pore volume available to water, V_{H_2O} (moisture capacity), of CRH samples, Ca-M and monoliths was determined by immersion of samples in water until complete saturation of pores with moisture, generally for 4 h. Then the weight amount of absorbed water referred to the weight of dry sample was calculated:

$$V_{H_2O} = (m_1 - m_0) : m_0,$$

where m_1 and m_0 are the weights of wet and dry samples, respectively.

Thermogravimetric analysis of CRH and CRH-based monoliths was made with a NETZSCH STA 449C instrument upon heating the 10 mg samples from room temperature to 1000 °C under air atmosphere at a ramp rate of 10°/min.

The XRD analysis of CRH, both initial and after the alkaline treatment, was made with a HZG-4C instrument (FRE/Berger Prazisionmechanik, Germany) using monochromated cobalt radiation in the 2θ angle range of 15–75°.

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

Carbon content in the samples was determined with a VARIO ELEMENTAR III elemental analyzer. Silicon content was measured by X-ray fluorescence spectroscopy using a VRA-30 analyzer equipped with a Cr anode of X-ray tube and by means of a SPRUT-001 energy dispersive analyzer.

Mechanical crushing strength of monoliths was tested with an MP-9C device (Russia) by measuring the force required to destruct a monolith fragment with diameter 10 mm and length 10 mm between two parallel planes. Strength (P, kg/cm^2) was calculated by the formula:

$$P = \frac{p}{S} = \frac{p}{(\pi D^2/4)},$$

where p is the indicator reading, kg; S is the cross-section area of monolith, cm^2; D is the diameter of monolith, cm.

3. Results and discussion

3.1. Rice husk carbonization and alkaline activation

Table 1 lists the gravimetric data on the weight loss of rice husk versus carbonization temperature. One may see from the tabulated data that changes in the sample weight gradually become more pronounced as the temperature rises; Δm increases from 21.4% at carbonization temperature of 400 °C to 49.2% at 800 °C. Samples carbonized at different temperatures strongly differed in their

Table 1
Weight loss of rice husk versus carbonization temperature.

Samples	Δm(%)
RH-400	21.4
RH-450	23.7
RH-500	29.3
RH-550	32.6
RH-600	35.9
RH-650	42.7
RH-700	46.1
RH-750	47.5
RH-800	49.2

external appearance. In particular, samples carbonized at temperatures up to 600 °C were dark brown rather than black in color. Presumably, at temperatures lower than 600 °C only the partial carbonization occurred, whereas heavy tars and low-molecular carbonaceous compounds are evolved at higher temperatures. As the pyrolysis temperature increases, so does the content of carbon phase in the samples (see Fig. 1).

For monoliths preparation, we chose the RH sample obtained by carbonization at 700 °C, the temperature at which the monoliths will be calcined. The CRH sample contains 49 wt.% of carbon and 17 wt.% of Si, the rest being represented by N, H, O and traces of K, Ca, Fe, Zn, Ti, Al, Cl, S, P, Cu, Ni and Mn.

First we studied the morphological and textural properties of CRH and explored the possibility of modifying the porous structure by alkaline treatment.

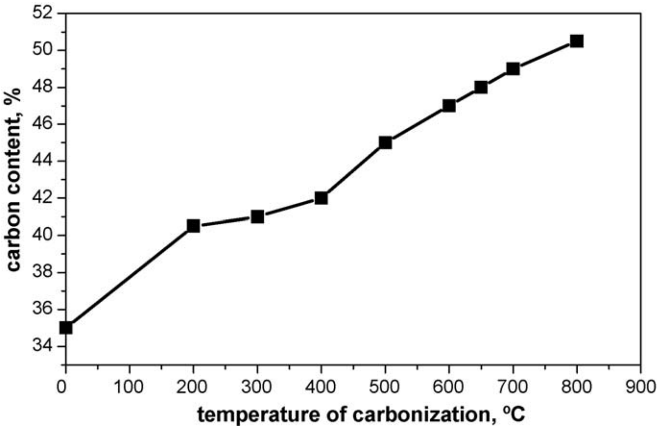

Fig. 1. Content of the carbon phase in carbonized rice husk versus the pyrolysis temperature.

The SEM images of RH sample carbonized at 700 °C are displayed in Fig. 2. Textural characteristics of the sample, BET specific surface area, pore volume available to water, volume of mesopores and micropores, and diameter of mesopores according to the nitrogen adsorption data are presented in Table 2.

One may see from the SEM images that macrostructural particles following the shape of rice husk form during carbonization. The particles are made of plate walls and virtually round channels of various size inside the plates (Fig. 2a). The

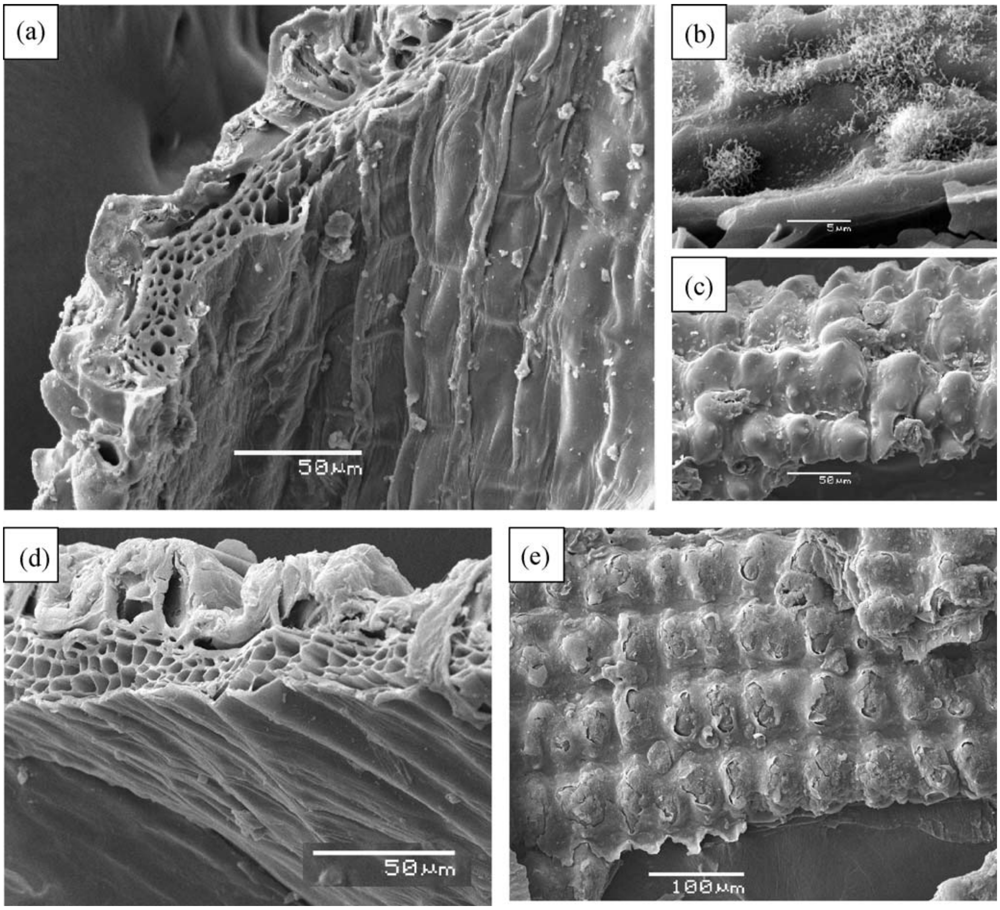

Fig. 2. SEM images of the rice husk carbonized at 700 °C: a—CRH cross-section showing the channel structure formed after removal of cellulose; b—carbon fibers on the CRH walls; c—the 'button-like' structure of CRH external surface; d and e—CRH after three operations of leaching with KOH solution.

Table 2
Dependence of textural properties of carbonized rice husk and monoliths prepared from it on a number of leaching operations and on the monolith preparation method.

No	Samples*	Number of operations leaching-alkaline agent	A_{BET} (m^2/g)	V_{H2O} (cm^3/g)	V_{Σ},/V_{μ} (cm^3/g)	Mesopore fraction (vol.%)	D_{pore} (nm)	P (kg/cm^2)
1	CRH-0	Before leaching	165	3.8	0.095/0.07	26	1.7	
2	CRH-1K	1-KOH	370	5.2	0.38/0.06	84	3.0	
3	CRH-3K	3-KOH	390	5.7	0.39/0.05	87	3.2	
4	CRH-4K	4-KOH	395	5.7	0.39/0.055	86	3.0	
Preparation of monoliths by scheme 1								
5	M1-0	Before leaching	120	0.44	0.09/0.04	56	2.3	60
6	M1-1 K	1-KOH	205	0.70	0.20/0.05	75	2.8	45
7	M1-2 K	2-KOH	260	0.76	0.26/0.046	82	2.9	40
8	M1-3 K	3-KOH	280	0.80	0.27/0.043	84	2.8	40
9	M1-4 K	4-KOH	350	0.85	0.32/0.05	84	2.7	29
10	M1-4 Na	4-Na_2CO_3	185	0.60	0.14/0.046	67	2.3	56
Preparation of monoliths by scheme 2								
11	M2-3 K	3-KOH leaching of initial components	306	0.89	0.28/0.042	85	2.7	23

*-samples designation: 1–4—CRH-lK, where CRH is carbonized rice husk; l—number of leaching operations; K-cation of an alkaline agent. 5–11—MN-lK, Na, where M is monolith; N—number of the scheme of monolith preparation; l—number of leaching operations; K, Na-cation of alkaline agent.

skeletal part of the particle is microporous; the nitrogen adsorption study revealed that ca. 75% of the porous space is occupied by micropores (see Table 2, sample 1). Morphology of the particle walls is uniform, dense, with local formation of carbon fibers on the surface (Fig. 2b). The presence of channels with diameter 5–10 μm in the CRH structure determines a remarkably high moisture capacity. External wall of the sample is structured by regular cambers (Fig. 2c), which are called button-like or bumps by the authors of [33]. According to the data reported in [33], the channels emerge from the rice husk pores upon removal of cellulose during pyrolysis, while the bumps form due to fast removal of volatile components from the particle surface.

Summing up the SEM and nitrogen adsorption data, one may conclude that the CRH sample comprises mainly the macropores of size 5–10 μm, micropores of size less than 17 Å, and a minor amount of mesopores.

The development of our method for alkaline treatment of CRH was based on the literature data. In [20,34] it was demonstrated that KOH is preferable for the preparation of carbon materials with high specific surface area and large pore volume, due to activation of the surface upon interaction of carbon with KOH by the reaction:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3. \qquad (1)$$

In the process, mainly the formation of microporous structure is facilitated.

In the case of silicone containing carbon composites the use of Na or K carbonates as alkaline agents [20,21] is another method to obtain mesoporous materials due to washing out from the matrix the water-soluble Na or K silicates forming by the reaction:

$$Me_2CO_3 + SiO_2 \rightarrow Me_2SiO_3 + CO_2, \qquad (2)$$

where (Me = Na, K), and SiO_2 serves as a template for pore formation.

In reported methods of impregnation or mechanical mixing of carbon material with an alkaline agent the weight ratio of KOH and K_2CO_3 (Na_2CO_3) to carbon material is 4:1 and 3:1, respectively. The treatment is performed in inert atmosphere at 650–1000 °C.

Taking into account the role of mesoporous structure in functionalization of monoliths, most preferable for us is the procedure of leaching by Na or K carbonates. However, the application of procedure including impregnation of monoliths in an excess of concentrated Na_2CO_3 solution, drying, and calcination at 700 °C in Ar atmosphere resulted in cracking of the monolith and appearance of the Na_2CO_3 thermal decomposition products on the external surface of monolith structure. Evidently the porous space of monoliths is insufficient for introduction of the Na_2CO_3 amount necessary for leaching, so this procedure is not convenient for monolith samples.

We assumed that the use of more reactive KOH at temperatures far lower than those reported in the literature would allow us to modify the porous structure by SiO_2 leaching accompanied by the formation of mesopores. Thus, further alkaline treatment of CRH and CRH-based monoliths was carried out at 80–100 °C using a 12% solution of potassium hydroxide.

As shown in Table 2, the application of this procedure considerably enhances all the parameters of CRH porous structure. Even after a single leaching operation, the specific surface area increases more than 2-fold, and the total pore volume increases nearly 4-fold (Table 2, sample 2). It is essential that the development of porous structure occurs mainly due to mesopores formation (Fig. 3) caused by silica removal from the matrix, which is confirmed by the Si content analysis of alkaline solutions and wash water. Note that main changes in the porous structure occur in a first leaching operation, and repeated treatment with KOH virtually does not change the porous structure (Table 2, samples 2–4). A similar dynamics of Si washing out of the CRH matrix is observed: main decrease of silicon concentration in the sample occurs in the first leaching operation (Fig. 4, curve 1). After three operations of KOH treatment, washing with water and drying under the IR lamp, the Si content in CRH sample decreases from 17 to 1.6%, while the carbon content increases from 50 to 81%.

Note that leaching enhances also the CRH moisture capacity from 3.7 to 5.7 cm^3/g, probably due to increasing the diameter of channels (macropores). However, the SEM study of CRH sample after three leaching operations (Fig. 2d) can give only an assumptive answer to this question. There are some changes in the morphology of CRH walls: due to removal of silicon from the wall surface they become more loose and brittle (Fig. 2d and e) as compared to the initial sample.

The XRD characterization of CRH samples before and after leaching did not reveal any significant changes in the samples structure. XRD pattern of the initial sample (Fig. 5, curve 1) of carbonized rice husk shows the first maximum in the

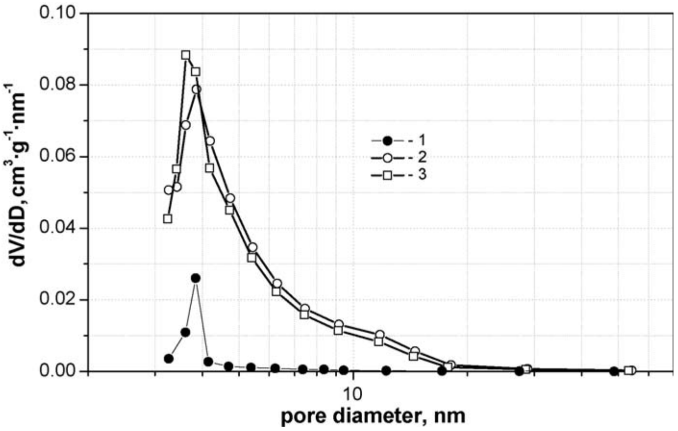

Fig. 3. Differential pore size distribution in CRH samples versus the number of leaching operations: 1—before leaching; 2—after single leaching; 3—after triple leaching.

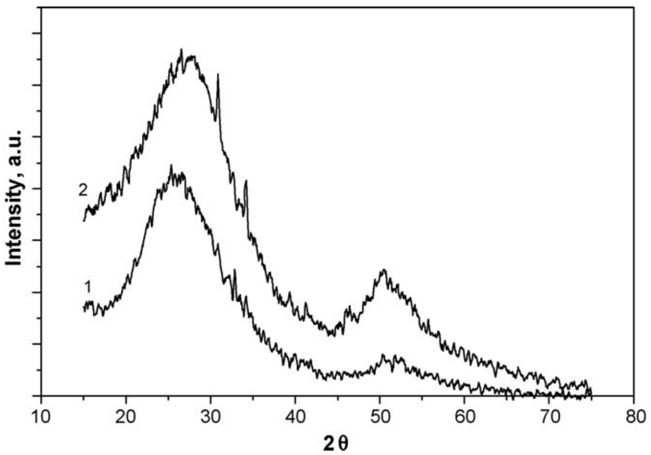

Fig. 5. Diffraction pattern of carbonized rice husk: 1—before leaching; 2—after triple leaching.

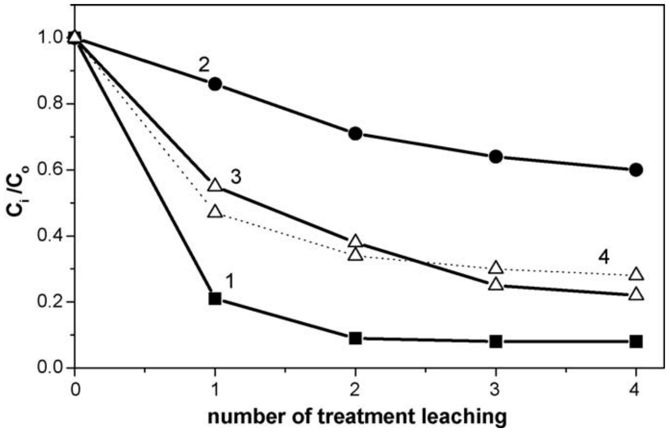

Fig. 4. The Si concentration versus the number of leaching operations in the samples: 1—CRH; 2—Ca-M; 3—experimental curve for CRH monolith (scheme 1); 4 (dots)—calculated curve for CRH monolith.

range of 18–35°, which is a superposition of the most intense maximum of amorphous SiO_2 ($2\theta = 22–26°$) and graphite-like material with interfacial distance $d/n = 3.86$ Å. After three leaching operations and SiO_2 removal from CRH, a maximum appears in the diffraction pattern (Fig. 5, curve 2), which virtually corresponds only to finely dispersed graphite-like carbon with $d/n = 3.81$ Å.

3.2. Monoliths preparation and alkaline treatment

Considering the effect of CRH to binder (Ca-M) ratio on plasticity of the molding material its composition was optimized and contains 60% of CRH and 40% of Ca-M in terms of the calcined substance. Our previous publications [27–30] 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.

We explored two schemes (Fig. 6) for preparation of monoliths with developed mesoporous structure from carbonized rice husk. By the first scheme, the monoliths were first produced from CRH and binder, dried, calcined, and only then

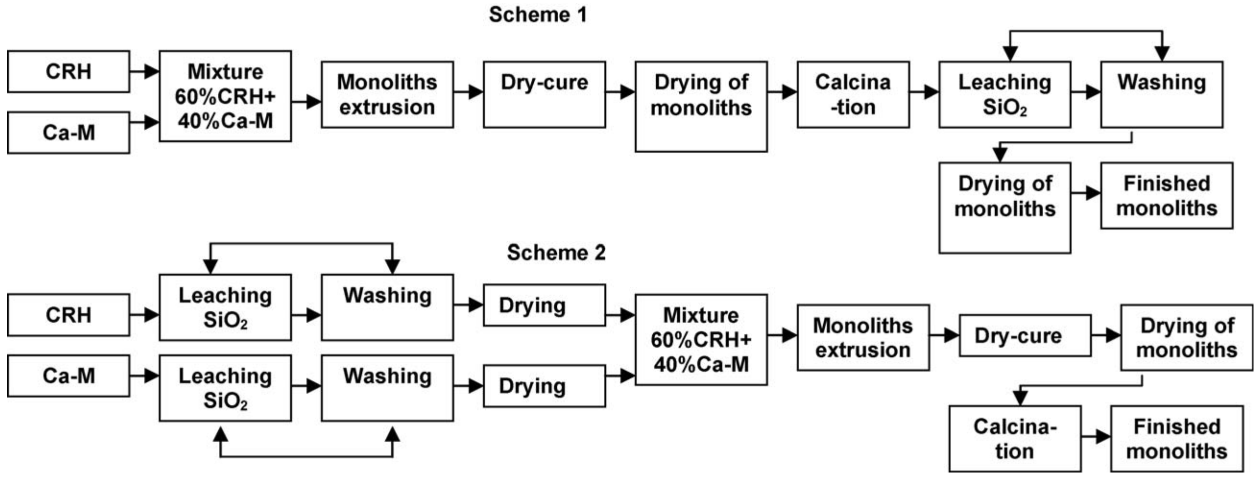

Fig. 6. Schemes of monoliths preparation including the step of leaching with KOH solution: 1—forming the monoliths from initial components followed by repeated treatment with KOH; 2—forming the monoliths from components pretreated with KOH.

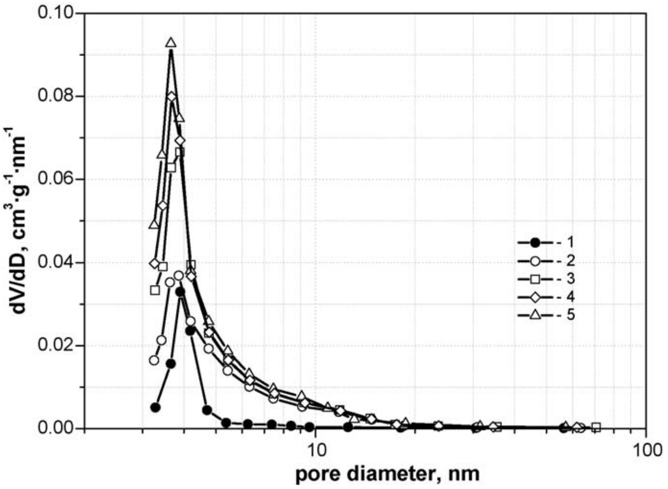

Fig. 7. Differential pore size distribution in CRH monolith samples prepared by scheme 1 versus the number of leaching operations: 1—before leaching; 2—after single leaching; 3—after double leaching; 4—after triple leaching; 5—after quadruple leaching.

treated repeatedly with KOH. Textural properties of the monoliths were tested after each treatment cycle (Table 2, samples 5–9). The KOH treatment enhances all the textural parameters of monoliths (pore volume available to water, volume of micropores and mesopores according to nitrogen adsorption, and BET specific surface area). Similar to the case of CRH itself, porous structure of monolith samples is developing mainly due to mesopores (Fig. 7); at that, in distinction to CRH material, parameters of the porous structure are enhanced gradually, increasing with each leaching cycle. A slower dynamics of SiO_2 removal from the monolith structure (Fig. 4) is related with the presence of Ca-montmorillonite, which contains bound silicon in alumosilicate composition. Experiments on SiO_2 leaching from monoliths by Na_2CO_3 solution revealed a lower efficiency of this alkaline agent as compared to KOH (Table 2, sample 10).

Fig. 8 shows a general view of CRH monolith. SEM images of cross-sections of monolith (Fig. 8b) and monolith material at high magnification (Fig. 8c) demonstrate that morphological properties of the material are determined by the morphology of monolith components, fragments of CRH and Ca-M. After silica leaching (the triple treatment with KOH), the sample morphology remains virtually the same by the SEM data (Fig. 8d), but becomes more defective due to SiO_2 removal from CRH and Ca-M. This is evidenced by a minor decrease in mechanical strength of monolith samples after each cycle of KOH treatment.

The monoliths preparation by scheme 2 (Fig. 6) includes preliminary triple treatment of CRH and Ca-M powders with KOH solution followed by washing with water after each leaching cycle, forming, drying, and heat treatment. The following steps are similar to the scheme 1: mixing, extrusion, seasoning, drying and calcinations. As a result, monoliths were produced having the porous structure parameters close to those of sample M1-3K which was prepared by scheme 1 and subjected to triple alkaline treatment (compare samples 8 and 11 from Table 2). These two samples produced by different schemes are characterized by close contents of carbon phase, which burning out is accompanied by exothermal effect in the range of 470–500 °C (TGA data, Fig. 9). However, sample M1-3K shows a much higher mechanical strength than sample M2-3K; it means that preliminary leaching of Ca-montmorillonite leads to loss its binding ability in the finished monolith.

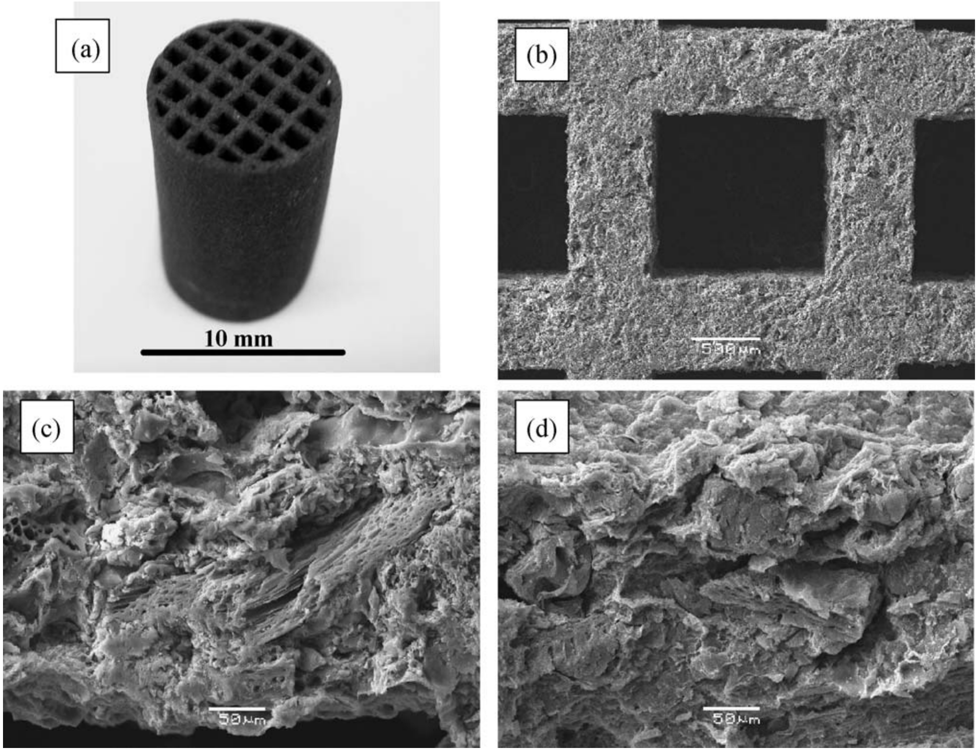

Fig. 8. CRH monoliths (scheme 1): a—external appearance of the monolith; b—SEM image of monolith partitions; c—SEM image of the monolith material before leaching; d—SEM image of the monolith material after triple leaching with KOH.

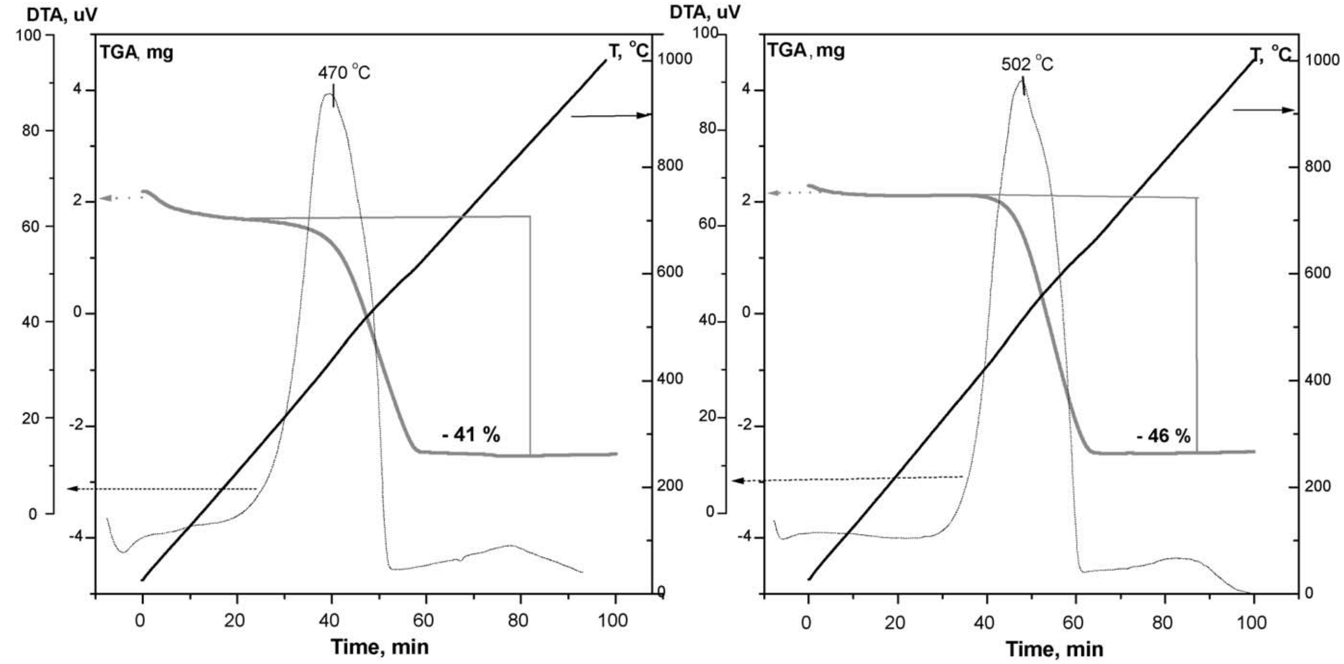

Fig. 9. TGA of CRH monolith samples: on the right—a monolith prepared by scheme 1 after triple leaching with KOH, weight loss due to carbon burn-out is 41 wt.%; on the left—a monolith prepared by scheme 2, weight loss due to carbon burn-out is 46 wt.%.

4. Conclusion

A method for preparation of monoliths from carbonized rice husk with developed mesoporous structure via modification of the porous structure by silica leaching has been developed. The effect of preparation procedure and treatment with alkaline agents, such as KOH and Na_2CO_3, on the chemical and textural properties of monolith samples was studied. Treating the monoliths with a 12% solution of KOH provides the development of mesoporous structure due to leaching out 70–75% of SiO_2 from the monolith material. After three cycles of KOH treatment and washing with water, the resulting monoliths have specific surface area of 280 m^2/g, pore volume determined from nitrogen adsorption as high as 0.3 cm^3/g, moisture capacity of 0.8 cm^3/g, and a rather high mechanical strength. These properties are appropriate for further use of the monoliths as catalyst supports and adsorbents.

Special interest was paid to CRH sample obtained by pyrolysis of rice husk at 700 °C in argon atmosphere. By the XRD data, the carbonized product is a finely dispersed graphite-like material containing X-ray amorphous silica. According to the SEM and nitrogen adsorption studies, CRH comprises mainly the macropores formed by 5–10 μm channels, micropores of size less than 17 Å, and a minor amount of mesopores. The channel structure of the macropores provides a high moisture capacity of CRH, ca. 4 cm^3/g. Treatment of the carbonized product with a 12% solution of potassium hydroxide leads to a 90–95% leaching of SiO_2 from the matrix material, increases the specific surface area from 167 to 400 m^2/g, and pore volume from 0.1 to 0.4 cm^3/g due to formation of mesoporous structure.

Acknowledgements

The authors are grateful to V.A. Ushakov for XRD analysis and interpretation, T.Ya. Efimenko for determination of textural properties, and G.S. Litvak for thermogravimetric measurements.

References

[1] V.N. Parmon, Z.R. Ismagilov, M.A. Kerzhentsev, in: J.M. Thomas, K.I. Zamaraev (Eds.), Catalysis for Energy Production. In Perspectives in Catalysis: Chemistry for 21st Century, Blackwell Scientific Publication, Oxford, 1992, p. 337.
[2] A. Cybulski, J.A. Moulijn, Catal. Rev. – Sci. Eng. 36 (2) (1994) 179.
[3] J.A. Moulijn, A. Cybulski, Structured catalysts and reactors, Marcel Dekker (1998).
[4] Z.R. Ismagilov, N.V. Shikina, S.A. Yashnik, S.R. Khayrulin, V.B. Koptenarmusov, A.A. Smislov, A.V. Polonik, Russian-International Conference of Catalytic Technologies of Environments Protection for the Industry and Transport, St. Petersburg, 11–14 December, (2007), p. 209.
[5] M.M. Yemuranov, V.A. Biisenbayev, Z.A. Mansurov, A.N. Sabitov, Zh.M. Basygaraev, S.A. Ibragimova, M.K. Gil'manov, Izvestiya NAS RK 3 (375) (2006) 76.
[6] Z.A. Mansurov, in: R. Gross et al (Ed.), Nonoscale-Devices–Fundamentals and Applications, Springer, 2006, p. 355.
[7] P. Brown, I.A. Jefcoat, D. Parrish, S. Gil, E. Graham, Adv. Environ. Res. 4 (1) (2000) 19.
[8] A. Sukla, Y.-H. Zhang, P. Dubey, J.L. Margrave, S.S. Sukla, J. Hazard. Mater. 95 (2002) 137.
[9] K. Conrad, H.C.B. Hansen, Biores. Technol. 98 (2007) 89.
[10] N. Fiol, I. Villaesscusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sep. Purif. Technol. 50 (2006) 132.
[11] B.M.W.P.K. Amarasinghe, R.A. Williams, Chem. Eng. J. 132 (1–3) (2007) 299.
[12] V.K. Gupta, I. Ali, J. Colloid Interf. Sci. 271 (2004) 321.
[13] T.C. Chuah, A. Jumasiah, I. Azni, S. Katayan, S.Y.T. Choong, Desalination 175 (2005) 305.
[14] Q. Feng, Q. Lin, F. Gong, S. Sugita, M. Shoya, J. Colloid Interf. Sci. 274 (2004) 1.
[15] Z.A. Mansurov, N.K. Zhylybaeva, P.S. Valieva, R.M. Mansurova, Chem. Sustainable Dev. 10 (2002) 321.
[16] F. Adam, J.H. Chua, J. Colloid Interf. Sci. 280 (2004) 55.
[17] E. Natarajan, A. Nordin, A.N. Rao, Biomass Bioenergy 14 (1998) 533.
[18] Y. Guo, S. Yang, K. Yu, J. Zhao, Z. Wang, H. Xu, Mater. Chem. Phys. 74 (3) (2002) 320.
[19] Y. Guo, K. Yu, Z. Wang, H. Xu, Carbon 41 (8) (2003) 1645.
[20] P.M. Yeletsky, V.A. Yakovlev, V.B. Fenelonov, V.N. Parmon, Kinet. Catal. 49 (2008) 708.
[21] P.M. Yeletsky, V.A. Yakovlev, M.S. Mel'gunov, V.N. Parmon, Micropor. Mesopor. Mater. 121 (2009) 34.
[22] K.M. de Lathouder, T. Marques Fló, F. Kapteijn, J.A. Moulijn, Catal. Today 105 (2005) 443.
[23] T. Valdés-Solís, G. Marbán, A.B. Fuertes, Micropor. Mesopor. Mater. 43 (2001) 113.
[24] Th. Vergunst, F. Kapteijn, J.A. Moulijn, Carbon 40 (2002) 1891.
[25] T.A. Nijhuis, A. Beers, T. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Catal. Rev. 43 (2001) 345.
[26] K.P. de Jong, J.W. Geus, Catal. Rev. Sci. Eng. 42 (2000) 481.
[27] S.A. Yashnik, Z.R. Ismagilov, I.V. Koptyug, I.P. Andrievskaya, A.A. Matveev, J.A. Moulijn, Catal. Today 105 (3–4) (2005) 507.

[28] S.A. Yashnik, I.P. Andrievskaya, O.V. Pashke, Z.R. Ismagilov, J.A. Moulijn, Catal. Ind. 1 (2007) 35.
[29] Z.R. Ismagilov, S.A. Yashnik, A.A. Matveev, I.V. Koptyug, J.A. Moulijn, Catal. Today 105 (3–4) (2005) 484.
[30] Z.R. Ismagilov, R.A. Shkrabina, N.V. Shikina, 4th Conf. Scientific Based for Preparation and Technology of Catalysts, Sterlitamak, Russia, 29 August–1 September, (2000), p. 131.
[31] Z.R. Ismagilov, International Seminar on Monolith Honeycomb Supports and Catalysts, St. Petersburg, (1995), p. 9.
[32] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control. Commercial Technology, VNR, New York, 1995, p. 206.
[33] A. Bharadwaj, Y. Wang, S. Sridhar, V.S. Arunachalam, Res. Commun. 87 (7) (2004) 981.
[34] M.A. Lillo-Rodenas, D. Cazorla-Amoros, A. Linares-Solano, Carbon 41 (2003) 267.