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Investigation of Silane Modified Ceramic Surface of Porous Mullite Ceramics

I. Markovska, F. Yovkova, G. Minov, D. Rusev, and L. Lyubchev

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Abstract**—**The present research focus on the processing of mullite-based ceramics from oil refinery industrial wastes and by-products of agricultural industry and on the investigating of silane modified surface of ceramics. Two waste products were used as initial material – waste aluminum oxide and waste rice husk. The burning - out additives used were waste rise husk. It is known that the oxide ceramics surface is hydrophilic due to the presence of – OH groups in it. The nature of ceramic surface regarding permeation of water and hydrocarbons can be changed by further treatment with silanes. The samples were studied mainly by X-ray analysis, FT-IR absorbance measurements and microscopic analysis. The X-ray analyses showed the phase composition depends on the firing temperature and on the purity of the starting alumina. Two kind of silanes were used for the transformation of surface from hydrophilic to hydrophobic – trimethoxymethylsilane (TMMS) and trimethylclorsilane (TMCS).

Keywords**—**Porous mullite ceramics, waste materials, trimethoxymethylsilane, trimethylclorsilane.

I. INTRODUCTION

NOWADAYS the recycling of industrial wastes to replace expensive oxide materials is paid significant attention on global scale. A perspective opportunity is the recycling of alumina widely used as either adsorbent or carrier catalyst in oil refineries, slag deposed by metallurgical and mining industries, etc. Gamma alumina (γ-Al_2O_3) is industrial waste from Lukoil Neftochim Co., Bourgas. It is used as adsorbent or carrier catalyst in several production lines of the company, so it is contaminated by different by type and amount impurities. After certain storage period (5 years) the unwanted material is moved to a depository for industrial waste on company territory. Rice husk is a by-product of rice milling process. Annually, about 500 mln tons of rice are processed to obtain 100 mln tons of rice husk [1]. The latter contain 70-75% organic components and the rest is inorganic components, mainly SiO_2 [2].

In previous works [3]-[6], the basic features of a mullite chemical processing was described. In connection with above mentioned, the aim of the present work is to obtain porous ceramic material using waste alumina and waste rice husk, which can be used as part of an apparatus for filtering and separation of liquids [7], emulsions and melts. Basically, the oxide ceramics is hydrophilic due to the presence of – OH groups in it. The nature of ceramic surface regarding permeation of water and hydrocarbons can be changed by further treatment with silanes [8]. Such additionally modified ceramics with trimethoxymethylsilane and trimethylclorsilane can be used for selective separation of emulsions.

II. EXPERIMENTAL

A. Methods

The apparent porosity was determined by the method of hydrostatic weighing. The methodology used was described in the [9].

The phase compositions of the porous materials synthesized were revealed by X-ray analysis. The X-ray analysis were carried out by the method of powder diffraction using X-ray apparatus IRIS – M, Germany equipped with goniometer URD-6 (Germany) and with CuKα radiation.

FT-IR spectra were recorded with a Tensor 27 Fourier transforms infrared spectrometer FTIR (Bruker, Germany). The spectral region between 4000 and 400cm^{-1} was scanned with a 4cm^{-1} resolution. Specimens prepared as KBr pellets were used.

The SEM photographs were taken using scanning electron microscope Tesla BS 340 (Czech Republic).

B. Raw Materials

Two types of industrial waste were used as initial materials - aluminum oxide from oil refining industry and rice husk from agricultural industry.

C. Processing of the Waste Al_2O_3

The following scheme for recycling of waste alumina granules was suggested in order to convert γ-Al_2O_3 into the stable α-form: Granules → Washing with water → Drying at 120°C→ Preheating at 1000°C, 1 hour → Crushing→ Milling → Heating at 1350°C for 1 hour.

The contents of impurities in the initial γ-Al_2O_3 and the product α-Al_2O_3 were determined by emission spectral analysis. The results obtained showed that the purity of the product α-Al_2O_3 was 99.47% while that of the initial γ-Al_2O_3 was 99.24%. The contents of impurities decreased after thermal treatment at 1000°C followed immediately by

Irena Markovska is with the Department of Silicate Tehnology, Assen Zlatarov University, Bourgas 8010, Bulgaria (e-mail: imarkovska@btu.bg).

Fila Yovkova is with the Department of Silicate Tehnology, Prof. Dr. Assen Zlatarov University, Bourgas 8010, Bulgaria.

Georgi Minov is with the Assen Zlatarov University, Bourgas 8010, Bulgaria.

Dimitar Rusev is with the Department of Electronics and Electrical Engineering, Assen Zlatarov University, Bourgas 8010, Bulgaria.

Lyubcho Lyubchev is with the Department of General Chemistry, Assen Zlatarov University, Bourgas 8010, Bulgaria.

treatment of the hot product with 4n HCl. The aluminum oxide processed by this technique was the initial material for the synthesis of ceramics.

D.Processing of the Waste Rice Husk

Rice husk (RH) was obtained from suburb areas of Pardjik, Bulgaria. Before use, the rice husk were thoroughly washed – three times with tap water followed by three times with deionised water to remove adhering soil, clay and dust, boiled for an hour to desorb any impurities and finally, dried at 100^0C overnight. The dried husk were ground in rotary cutting mill and sieved manually with 0.63–0.12mm sieves. This starting material was used for all further studies.

The amorphous SiO_2 was obtained by heat treatment of raw rice husk. Many authors sustain the opinion that almost pure SiO_2 can be obtained due to its high content in the husk (13-29 mass. % SiO_2) [10]-[13]. The analyzes carried out show that the raw material used in this work contain 23, 82% SiO_2. For the experiment's purpose raw rice husk were burned in air at 500°C. Under these conditions a gray ash (GRH) which contains simultaneously C and SiO_2 was obtained. Upon further heating by high temperature burning CO_2 has been released and additional porosity in ceramics had been prepared.

E. Experimental Procedure

A series of ceramic materials were synthesized based on pure α-Al_2O_3 with a purity of 99.9% and recycled α-Al_2O_3 by the petrochemical industry in the amount of 70 mass %. As the second component, 30% gray husk which contains amorphous SiO_2, obtained by heat treatment of raw rice husk at 500^0C for 1 hour was used. Table I shows the synthesized compositions.

TABLE I
COMPOSITION OF THE SYNTHESIZED SAMPLES

Composition №	Al_2O_3 recycled / pure, %	Gray rice husk, %	Synthesis temperature, ^{0}C
1	70 % recycled	30	1350^0C
2	70 % pure	30	1450^0C
3	70 % recycled	30	1450^0C

Studies carried out have shown rice husk heating at 500^0C in air medium gave the fully amorphous product (Fig. 1).

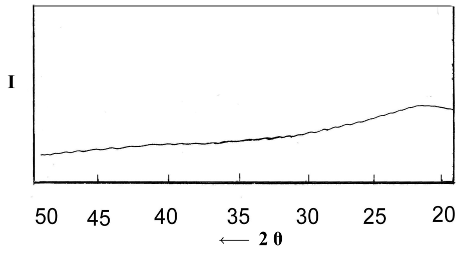


Fig. 1 X- ray data of rice husk burned at 500^0C in air

III. RESULTS AND DISCUSSION

The samples were prepared by semi-dry pressing on a double-action press (Carl Zeiss Jena, Germany. As plastifier 8 % aqueous solution of polyvinyl alcohol was used. The high - temperature sintering of the sample was carried out at 1350^0C and 1450^0C in air with 90min soaking at maximum temperature.

Fig. 2 presents phase diagram of the alumina - silica system [14], [15]. As can be seen from it the only chemical compound produced by the reaction of α-Al_2O_3 and SiO_2 is the mineral mullite ($3Al_2O_3.2SiO_2$).

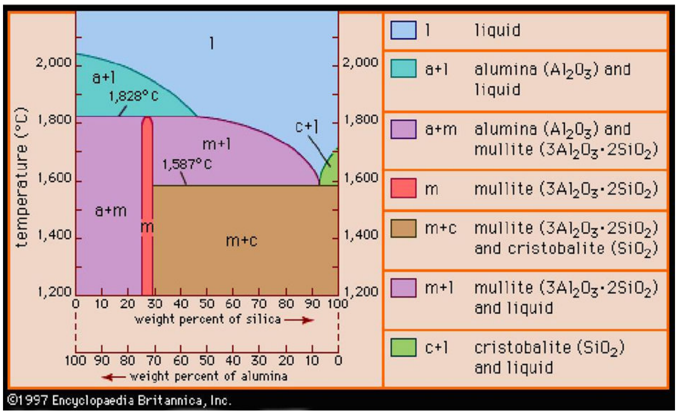


Fig. 2 Phase diagram of the alumina – silica system

By the method of X-ray diffraction analysis the phase composition of the synthesized materials was studied. The results obtained are in good agreement with the above mentioned diagram (Table II). Mainly three phases with different percentages for compositions 1÷3 were formed, where mullite is primary phase and corundum and cristobalite - the secondary phases (Table II).

TABLE II
MAIN CRYSTAL PHASES IN THE SAMPLES

sample №	phase composition	quantity, %
1	Mullite	49,95
	Corundum	38,97
	α- cristobalite	11,08
2	Mullite	67,97
	Corundum	22,09
	α- cristobalite	7,11
	other phases	2,83
3	Mullite	62,41
	Corundum	27,28
	α- cristobalite	9,31
	other phases	1,00

The sintering temperature affects mullite formation and sintering. The expansion resulting from the formation of primary and secondary mullite and the shrinkage resulting from the sintering, affect the pore characteristics and the strength. During the high temperature sintering, the silicon dioxide of the husk reacts with the aluminum oxide matrix to form needle-like mullite crystals (Fig. 4) while the other part transforms into cristobalite preserving the general shape of the thermally treated rice husk. This fact should be attributed not only to the newly formed mullite phase but also to the specific spring-like structure of the three dimensional structural chains of the silicon-oxygen tetrahedrons which absorb and quench the tensions (Fig. 3).

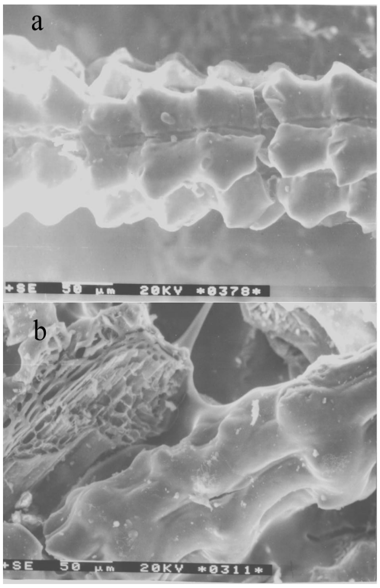


Fig. 3 Three dimensional structural Si-O chains in GRH

The needle-like mullite crystals obtained as a result of the interaction between the corundum matrix and silicon dioxide contained in the burned husk can be seen in Fig. 4. Fig. 4 shows that the mullite is occur in the form of radial-ray aggregates composed of needle-like crystals with a length of about 25µm.

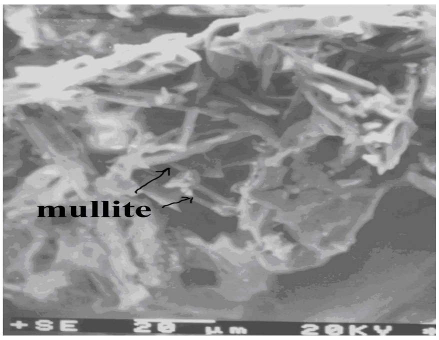


Fig. 4 SEM photograph shows needle-like mullite crystals

It was found that the heat resistance of the sample is directly depending on the prevailing phases due to the difference in the coefficient of linear thermal expansion (CLTE) of corundum, quartz, cristobalite and mullite - resp. CLTE of corundum is $7.5\text{-}8.5x10^{-6}C^{-1}$ ($20\text{-}1000^{0}C$), of mullite $–5x10^{-6}C^{-1}$ ($20\text{-}1000^{0}C$), of quartz $-0.5x10^{-6}C^{-1}$. In this connection a sample with a large amount of formed mullite phase have significantly better thermal stability than those with little one.

Some basic physico-mechanical properties of the samples synthesized were determined. The data on density, porosity and water absorption are presented in Table III.

TABLE III
PHYSICO-MECHANICAL PROPERTIES OF SAMPLES

sample	water absorption, %	porosity $_{app}$, %	ρ_{app}, g/cm^3
1	35,23	58,31	1,69
2	33,65	53,45	1,73
3	31,56	52,23	1, 87

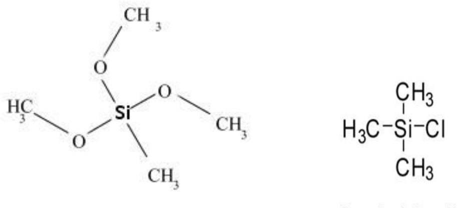
Defined physical and mechanical properties of the synthesized materials show that last successfully substitute this materials for production of filter elements.

A special vertical reactor for separation of emulsions was developed for this purpose (Fig. 5). The reactor is filled with hydrophilic and hydrophobic components for separation of water-oil emulsions.

Fig. 5 Installation with vertical reactor to filter emulsions

A. Silane Modified Ceramic Surface of Porous Mullite Ceramics

In order to separate the water from the organic phase in the emulsions it is necessary to create ceramic filler with hydrophilic and hydrophobic surfaces. It is known that the oxide ceramics is hydrophilic due to the presence of - OH groups in it. By treatment with silanes ceramic surface was converted from hydrophilic to hydrophobic. Two kind of silanes were used for the transformation of surface from hydrophilic to hydrophobic – trimethoxymethylsilane (TMMS) and trimethylclorsilane (TMCS) (Fig. 6):



Trimethoxymethyl silane

trimethylclorsilane

Fig. 6 Formula of compounds: trimethoxymethylsilane (TMMS) and trimethylclorsilane (TMCS)

Fig. 7 presents samples treated with trimethoxymethyl silane and Fig. 8 shows the samples treated with trimethylclorsilane.

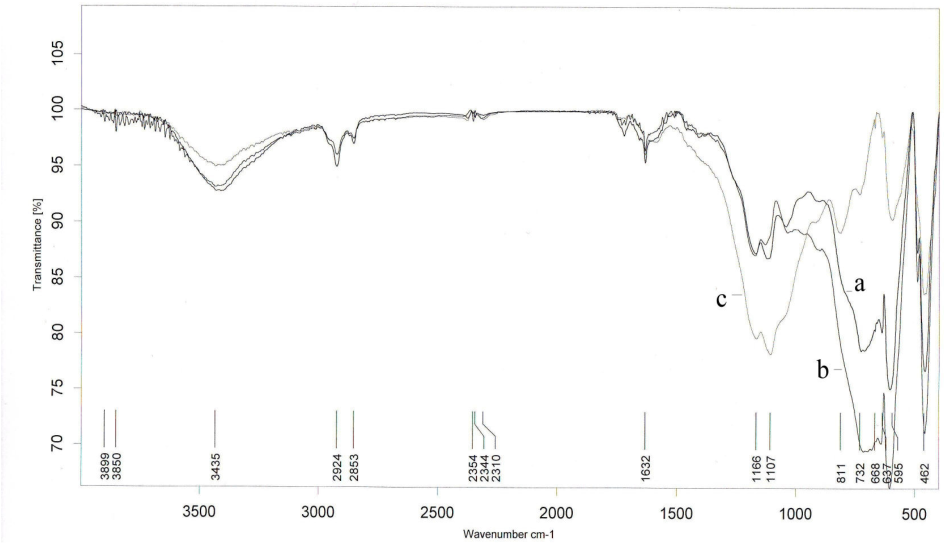


Fig. 7 Samples treated with trimethoxymethyl silane: a) untreated specimen, b) composition 3, c) composition 2

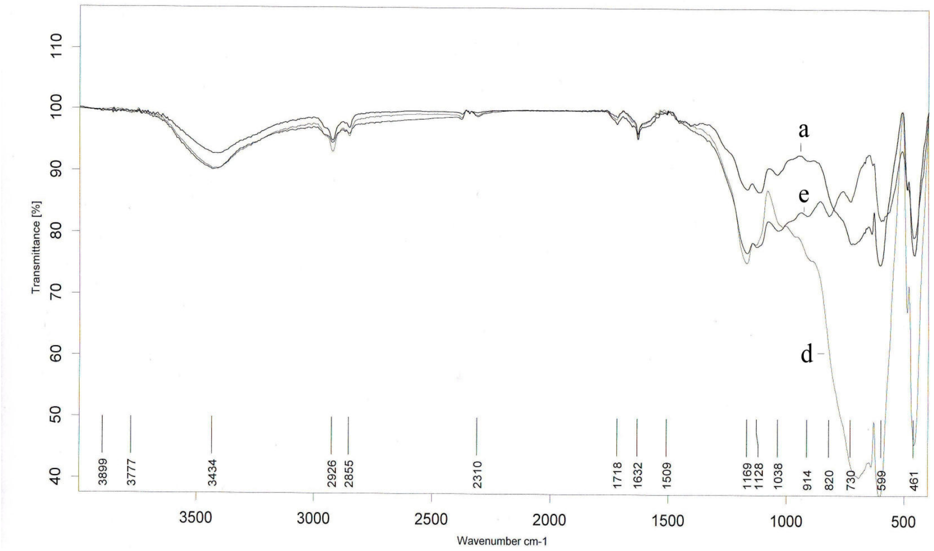


Fig. 8 Samples treated with trimethylclorsilane: a) untreated specimen, d) composition 3, e) composition 2

The major bands that appeared in the two FTIR spectra are as follows: in Fig. 7 at 3435cm^{-1}, 2924cm^{-1}, 2853cm^{-1}, 1632 cm^{-1}, 1166cm^{-1}, 1107cm^{-1}, 811cm^{-1}, 732cm^{-1}, 668cm^{-1}, 637cm^{-1}, 595cm^{-1}, 462cm^{-1} and in Fig. 8 – at 3434cm^{-1}, 2926cm^{-1}, 2855cm^{-1}, 1718cm^{-1}, 1632cm^{-1}, 1166cm^{-1}, 1128cm^{-1}, 1038cm^{-1}, 914cm^{-1}, 820cm^{-1}, 730cm^{-1}, 599cm^{-1}, 461cm^{-1}. In two figures at about 3434/3435 cm^{-1} (medium) was observed a broad band which corresponds to the (O-H) stretch of hydrogen bonded -OH groups to ceramic surface. The presence of water is confirmed by the strong (O-H) deformation band at 1632cm^{-1} which was assigned to the deformation vibration of O-H in H_2O. Bands at about 3000 cm^{-1} due to C-H bonds: at 2924cm^{-1} / 2926cm^{-1} due to $v_{\text{as}}(CH_3)$, and at 2853cm^{-1} / 2855 cm^{-1} – due to v_s (CH_3). The high – frequently peaks in the spectral range 1166 - 730cm^{-1} correspond to Si-O stretching modes in SiO_2 from $3Al_2O_3$.$2SiO_2$ while the peaks in the spectral range 800-600cm^{-1} and 461/462cm^{-1} correspond to Al-O bond in mullite too.

Figs. 9 and 10 show that after contacting the mullite surface with TMMS and TMCS, the spectrum appears deeply modified. First of all weakening lines of the sharp -OH stretching bands of the surface hydroxyl groups, that are likely involved in the adsorption. The presence of intense absorption bands in the C—H stretching and bending region 2900 - 2850 cm^{-1} at FTIR spectra in Figs. 9 and 10 provides evidence for the formation of TMCS and TMMS species on the ceramics. The Fig. 9 presents possible reaction schemes between mullite surface and TMCS, while Fig. 10 presents reaction schemes between mullite surface and TMMS.

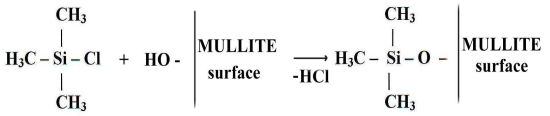


Fig. 9 Possible reaction schemes between ceramics and TMCS

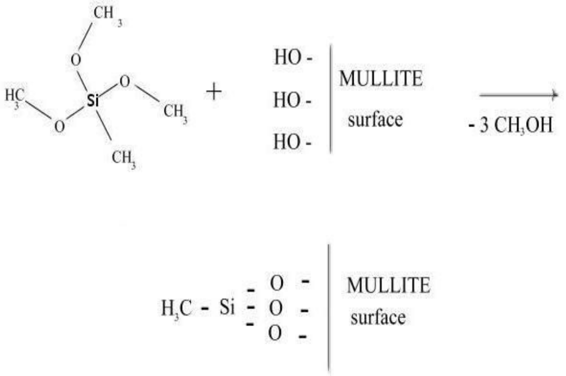


Fig. 10 Possible reaction schemes between mullite and TMMS

According these mechanisms is formed one and three - covalent bonds on the ceramic surface and by this way it becomes from a hydrophilic → into hydrophobic.

IV. CONCLUSION

A porous mullite ceramic material was obtained by the method of burning-out additives. Two waste products were used as initial material – waste aluminum oxide and waste rice husk. The burning of rice husk in air gives almost pure SiO_2 – 94.47%. For the purpose of the experiment was used pure as well as recycled alumina. The raw rice husk was burned in air at 500 °C and a gray ash obtained contains simultaneously C and amorphous SiO_2.

The sintering temperature affects mullite formation and sintering. The X-ray structural analysis showed that the main phases in the samples obtained were mullite, corundum and cristobalite.

The hydrophilic character of oxide ceramic surface can be changed into a hydrophobic one by grafting trimethoxymethylsilane (TMMS) and trimethylclorsilane (TMCS) on the surface on the ceramics. FTIR spectra show that after contacting the mullite surface with TMMS and TMCS, the spectrum appears deeply modified. The product is a TMCS and TMMS species on the ceramics where a single and three - covalent bridge is formed. Thus, the formation of this species does allow hydrophobization of the ceramic surface.

The main properties of synthesized materials are good thermal shock stability and corrosion resistance even at high temperatures. This kind of ceramics is chemically and thermally stable up to approximately 1200°C. The high porosity (over than 50%) of these mullite-based materials determined their potential applications as a filters.

The hydrophobic and hydrophilic components can be used as filler in the reactor particularly developed for this purpose.

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