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INFLUENCE OF SURFACE MODIFICATION ON MORPHOLOGY AND PHYSICOCHEMICAL PARAMETERS OF SYNTHETIC MAGNESIUM SILICATE

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Studies on surface modification of synthetic magnesium silicates were presented. Magnesium silicate was obtained by precipitation reaction using solutions of magnesium sulphate and of sodium metasilicate. In the course of the synthesis, the reactive system was supplemented with agents capable of modifying the surface of synthetic magnesium silicate. For the purpose appropriate amounts of silane proadhesive compounds and of non-ionic surfactants were used. For the so obtained products physicochemical parameters were established, such as bulk density, capacity to absorb water (wettability with water), capacities to absorb dibutyl phthalate an paraffin oil, elemental composition, particle diameters, specific surface area and sedimentation tendency.

Key words: synthetic magnesium silicate, surface modification, silane coupling agents, adsorption isotherms

INTRODUCTION

The most frequently applied monocomponent mineral adsorbents include silica gels, active aluminium oxide, hydroxides and oxides of zirconium, titanium, iron, chromium, magnesium and zeolites. The above mentioned oxide adsorbents form principal components of mineral adsorbents and catalysers.

In order to widen the adsorptive techniques, apart from in already known adsorbents new adsorbents are designed, e.g., porous organosilicon polymers, porous salts, etc. The so called mixed systems found a relatively wide application. They constitute mixtures of two or more adsorbents, the structural-adsorptive properties of

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which differ from properties of individual components and of their mechanical mixture. A significant role is played also by silica fillers, which include highly dispersed powders representing amorphic silicas or mixtures of silica with calcium, aluminium, aluminium-sodium, magnesium or zinc silicates obtained in a chemical process or by processing of certain natural materials, which find application as an insoluble component of rubber mixtures and similar organic polymers (Krysztafkiewicz 1983).

Silicate fillers are obtained in a reaction of sodium silicate with a soluble salt of the appropriate metal. Following coagulation and activation the precipitated sediment is subjected to filtration, washing, drying, grinding. In few cases the dispersed material is subjected to compaction (Suda 1999, Krysztafkiewicz 1980, 1986, 1990, Stechman 2002).

In general, silicate fillers represent not defined chemical compounds but rather mixtures of a variable but defined ratio of SiO_2 to metal oxide, additively bound to silicone dioxide. Therefore, in character of their surface they resemble precipitated silica fillers.

Components of the SiO_2-MgO system easily react with each other, yielding magnesium silicate. Magnesium silicate is used for decolorization of petrolium lubricating oils, in thin layer chromaotography it is used for separation of substance mixtures extracted from biological material with the aim to estimate the remains of pesticides (Biziuk 2001, Nejmark 1988).

Functional groups significantly affect surface properties, which are decisive for directions of precipitated silica application. Physical structure and surface properties of silicates can be modified in the course of their production by adequate control of precipitation parameters, such as temperature and reaction time, pH, dosing rate and concentration of reagents, concentration of electrolytes, mixing rate and by final processing using various modifiers (Stechman 2002, Krysztafkiewicz 1986).

EXPERIMENTAL

MATERIALS

Synthetic magnesium silicate was obtained in a precipitation reaction using 5% magnesium sulphate solution and sodium metasilicate (5% aqueous solution in respect to SiO_2 content). Sodium metasilicate solution manifested the following parameters: Na_2O=8.8 %; SiO_2=28.5 %, density=1.38 g/dm^3 and the module of 3.33. The following modifying agents were used for surface modification of magnesium silicate: nonylphenylpolioxyethylene glycol ethers, Rokafenol N3, N6, N9 of a general formula $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$ (where $n_{av}=3$; $n_{av}=6$; $n_{av}=9.7$ for the respective Rokafenols) and oxyethylated unsaturated fatty alcohols, Rokanols K3 and K7 of the general formula $RO(CH_2CH_2O)_nH$ $R=C_{16\text{-}22}$, where $n_{av}=3$; $n_{av}=7$ for the respective Rokanols) from the group of non-ionic surfactants produced by the Rokita Chemical

Works and silane proadhesive compounds, U-311 (3-chloro-propyltrimethoxysilane), U-511 (3-methacryloxypropyltrimethoxysilane), U-611 (vinyltrimethoxysilane), U-222 (n-octyltriethoxysilane) and U-15 (N-2-aminoethyl-3-aminopropyl-trimethoxysilane), produced by UniSil company in Tarnów, Poland.

METHODS OF STUDIES

At the first stage of the studies magnesium silicate was precipitated using 5% solutions of magnesium sulphate and sodium metasilicate. The reaction was conducted in a 250 cm^3 flask equipped with a rapidly shafted stirrer. The reactive system maintained stable temperature. The flask was charged with 100 cm^3 5% solution of magnesium sulphate and the same amount of sodium metasilicate solution was dosed to the flask. The process was conducted at the temperature of 20, 40, 60 or 80°C.

Following dosing of the appropriate amount of sodium metasilicate the reactive system continued to be stirred for another 15 min. At the time modifying agents were added at 1; 3; or 5 weight parts. This involved the so called wet modification.

For all samples particle diameter, bulk density, capacities to absorb water and appropriate organic agents were determined. A sample of unmodified magnesium silicate was additionally analysed for its elemental composition and, using X-ray analysis, for its crystalline structure.

Taking advantage of ZetaPlus apparatus (Brookhaven Instruments Inc., USA) particle sizes and tendency for their agglomeration were estimated. The studies were conducted using dynamic light scattering technique.

In order to examine surface pattern of the obtained magnesium silicate its selected samples were examined by scanning electron microscopy (Philips SEM 515 instrument).

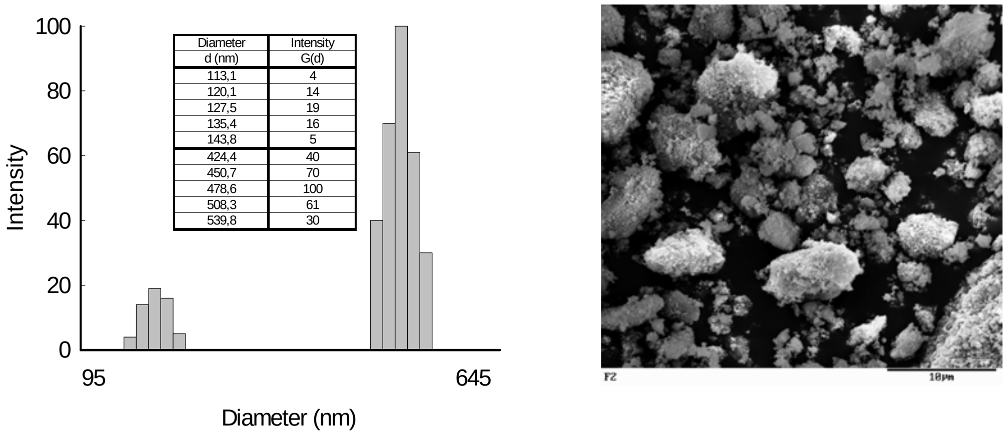
In selected samples of precipitated silicates specific surface area was estimated, by BET technique, as well as diameter and volume of pores. The measurements were performed using ASAP 2010 instrument (Micromeritics Instruments Co., USA).

SiO_2 content in unmodified magnesium silicate samples was estimated by weighing and the filtrate originating from the technique was tested for the content of magnesium, calcium, sodium, potassium using the ASA technique. The obtained results were converted to proportional content of individual metal oxides in samples of magnesium silicate, taking into account the amount of analysed filtrate and molar weights of the oxides.

Crystalline structure of unmodified magnesium silicate was studied by X-ray technique. Diffraction patterns were recorded in a horizontal TUR–M–62 diffractometer, equipped with the type HZW-3 goniometer. In order to obtain the radiation intensity distribution curve, $I=f(\Theta)$, a counting rate meter was used, electronically coupled to a graphic plotter.

RESULTS AND DISCUSSION

Particle size distribution and SEM photograph of synthetic magnesium silicate, precipitated at the temperature of 40°C are presented in Fig.1.



Diameter d (nm)	Intensity G(d)
113,1	4
120,1	14
127,5	19
135,4	16
143,8	5
424,4	40
450,7	70
478,6	100
508,3	61
539,8	30

a) b)

Fig. 1. a) Particle size distribution and b) SEM microphotograph of magnesium silicate

In the particle size distribution two bands could be noted. The first band corresponded to magnesium silicate particles of lower diameters, ranging from 113.1 to 143.8 nm (maximum intensity of 19 corresponded to particles of 127.5 nm in diameter). The other band of 424.4 to 539.8 nm represented particles of higher diameters, reflecting presence of aggregates in the examined sample (maximum intensity of 100 corresponded to the particle diameter of 478.6 nm). The mean particle diameter was 420.2 nm, and polydispersity amounted to 0.246. SEM photograph (Fig.1b) confirmed the presence of low diameter particles, which coalesced into higher particle clumps (aggregates and agglomerates).

Elemental composition of unmodified magnesium silicate samples is presented in Table 1.

Table 1. Elemental composition of magnesium silicates

Temperature (˚C)	SiO_2 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	Global humidity (%)	Bounded humidity (%)
20	62,5	10,69	0,21	0,93	0,021	25,4	15,0
40	64,1	13,30	0,52	0,30	0,012	23,4	12,6
60	63,7	13,09	0,35	1,08	0,053	24,2	14,2
80	62,5	12,47	0,51	2,07	0,011	24,0	11,6

The content of metal oxides in magnesium silicates precipitated at various temperatures, established by ASA technique and bound moisture content in the above samples are presented in Table 1. The content of magnesium oxide in the obtained silicates ranged from 10.69 % (precipitation temperature: 20˚C) to 13.30 % for the sample precipitated at 40˚C. The total content of calcium, sodium and potassium oxides did not exceed 3%. Presence of the metal oxides in the sample pointed to inaccurate washing of the sediment from remains of salts following precipitation of magnesium silicate. The relatively high content of bound moisture, ranging from 11.6% in the sample precipitated at the temperature of 20˚C to 15.0 % in the sample precipitated at the temperature of 80˚C pointed to presence of silanol groups in the internal structure of the obtained magnesium silicates.

Proportional content of silicon dioxide in magnesium silicate samples, as related to precipitation temperature, is presented in Fig.2.

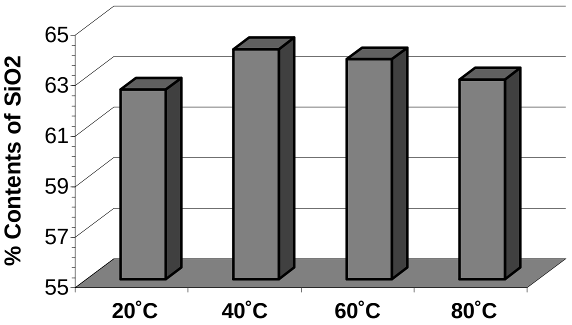


Fig. 2. SiO_2 content in magnesium silicate samples related to precipitation temperature

In all the cases, the content of SiO_2 in the sample ranged between 62.5% and 64.1 %. Thus, variation in composition for samples obtained in different temperatures was negligible. The highest SiO_2 content (64.1% SiO_2) was noted for the magnesium silicate sample precipitated at the temperature of 40˚C. The next is sequence were the sample obtained at the temperature of 60˚C (63.7% SiO_2), and that obtained at 80˚C (62.9% SiO_2). The lowest content of SiO_2 showed the sample precipitated at 20˚C (62.5% SiO_2).

A diffractogram prepared for the sample of synthetic magnesium silicate, precipitated at 40ºC with no additional surface modification is presented in Fig.3.

The performed X-ray studies demonstrated that the obtained magnesium silicate showed an amorphic form. Analogous diffractograms were obtained for the magnesium silicate samples precipitated at the temperatures of 20, 60 and 80˚C.

Surface modification of synthetic magnesium silicates using appropriate modifying substances was performed in order to improve their physicochemical properties. Particle size distribution and SEM photograph of magnesium silicate modified with 3 weight parts of Rokafenol N3 is presented in Fig.4.

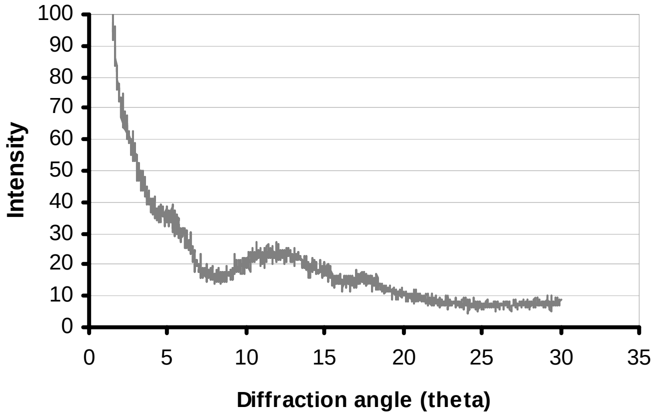
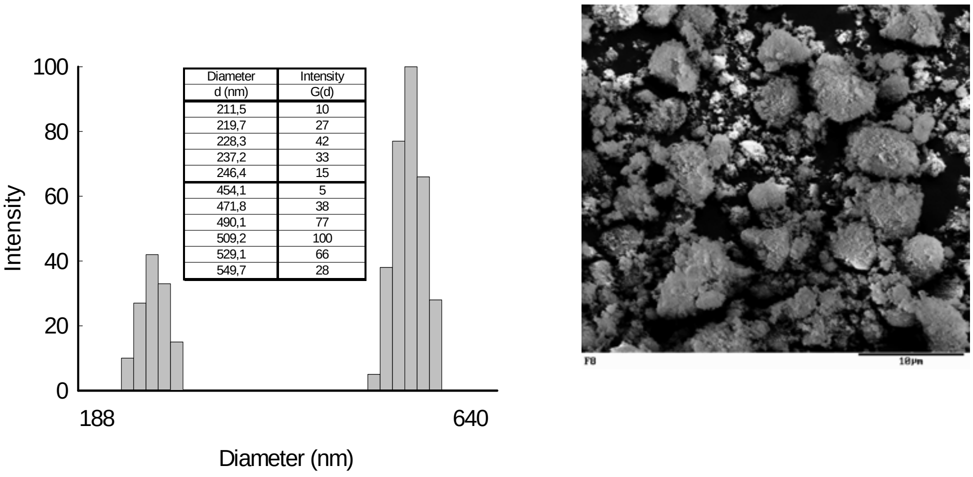


Fig. 3. Diffractogram of magnesium silicate sample precipitated at 40°C

As evident from the particle size distribution curve, the silicate sample was not fully uniform. The distribution manifested two bands of different intensity. The first, more intense band could be ascribed to primary particles of magnesium silicate; it spanned the range of 211.5-246.4 nm (maximum intensity of 42 corresponded to the particles of 228.3 nm in diameter). The other band of the particle size distribution corresponded to primary agglomerates (aggregates) of 454.1-549.7 nm in diameter (maximum intensity of 100 corresponded to aggregates of 509.2 nm in diameter). The mean particle diameter was 426.7 nm, and the polydispersity amounted to 0.198.

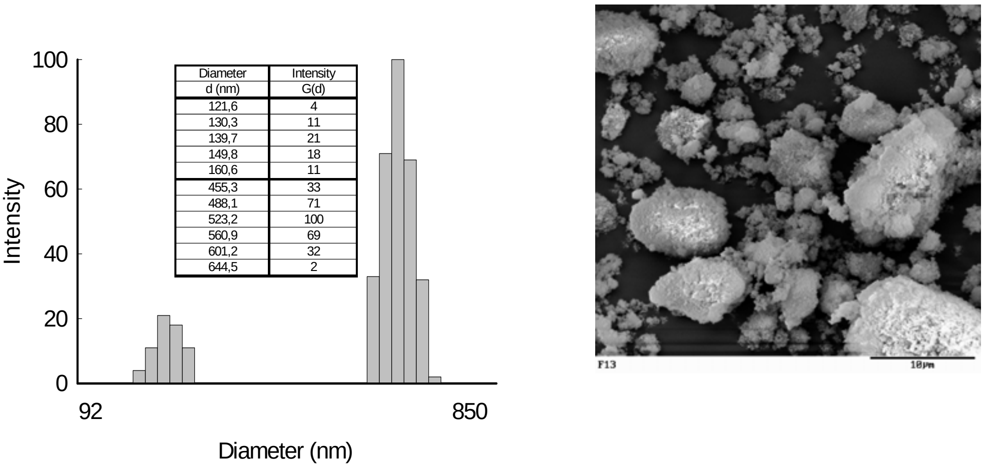


Diameter d (nm)	Intensity G(d)
211,5	10
219,7	27
228,3	42
237,2	33
246,4	15
454,1	5
471,8	38
490,1	77
509,2	100
529,1	66
549,7	28

a) b)

Fig. 4. a) Particle size distribution and b) SEM microphotograph of magnesium silicate modified with 3 w/w of Rokafenol N3

Particle size distribution and SEM photograph of magnesium silicate modified with 3 weight parts of the U-311 silane are presented in Fig.5.



Diameter d (nm)	Intensity G(d)
121,6	4
130,3	11
139,7	21
149,8	18
160,6	11
455,3	33
488,1	71
523,2	100
560,9	69
601,2	32
644,5	2

a) b)

Fig. 5. a) Particle size distribution and b) SEM microphotograph of magnesium silicate modified with 3 w/w of U-311 silane

Also in this case two bands of various intensity were present. The first of them spanned the diameter range of 121.6 nm to 160.6 nm (maximum intensity of 21 corresponded to silicate particles of 139.7 nm in diameter). The other band of the range of 455.3 nm to 644.5 nm represented larger particles, the so called primary aggregates (maximum intensity of 100 corresponded to the particles of 523.2 nm in diameter). In this case the mean particle diameter was 458 nm and the polydispersity amounted to 0.220.

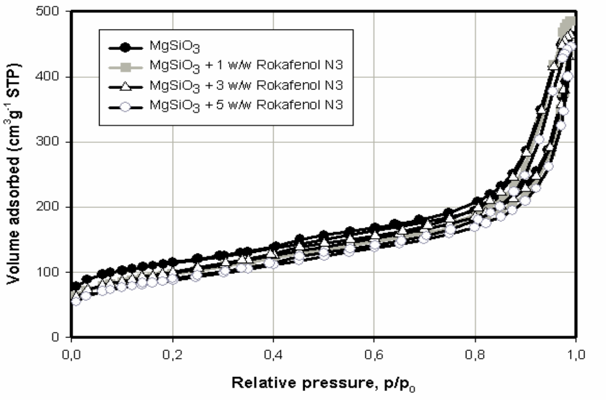


Fig. 6. N_2 adsorption/desorption isotherms of the examined magnesium silicates.

Isotherms of nitrogen adsorption and desorption for the unmodified magnesium silicate and for magnesium silicate modified with 1, 3 or 5 weight parts of Rokafenol N3, precipitated at 40˚C are presented in Fig.6. Shape of the isotherms obtained for the modified samples corresponded to that of the isotherm obtained for the unmodified silicate. The amount of adsorbed nitrogen increased smoothly till the relative pressure of 0.8 was reached. At higher values of the relative pressure an abrupt increase was observed in the amounts of adsorbed nitrogen. Such course of the curves pointed to high activity of the silicates. At p/p_o=1 the adsorbed amount of nitrogen reached the value of 460 cm^3/g for the unmodified silicate and for the silicate modified with 3 or 5 weight parts of Rokafenol and of 480 cm^3/g for magnesium silicate modified with 1 weight part of Rokafenol N3. The course of adsorption isotherms indicated that the magnesium silicates belonged to mesoporous substances (the amount of adsorbed nitrogen practically did not increase until relative pressure reached the value of 0.7). On the other hand, significant differences were evident in BET specific surface area. For the unmodified silicate the area amounted to 399 m^2/g, for the silicate modified with 1 weight part of Rokanol N3 it was 341 m^2/g, for the silicate modified with 3 weight parts of the compound it was 350 m^2/g and for the silicate modified with 5 weight parts of the compound it was 312 m^2/g.

Isotherms of nitrogen adsorption/desorption for the unmodified silicate, precipitated at 40˚C and for the magnesium silicate modified with 3 weight parts of Rokanol N3 or U-311 silane are shown in Fig.7.

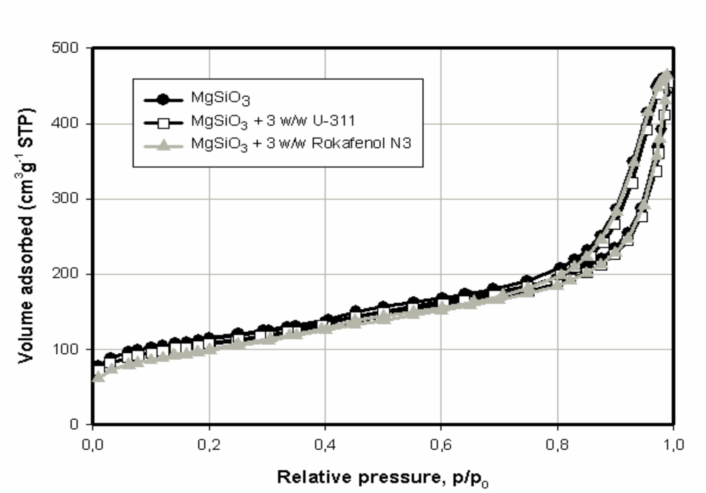


Fig. 7. N_2 adsorption/desorption isotherms of the examined magnesium silicates

The character of the isotherms was analogous to those presented in Fig.6. The amount of nitrogen adsorbed on magnesium silicate modified with 3 weight parts of 3-chloro- propyltrimethoxysilane (U-311) reached the value of 455 cm^3/g at the relative pressure of 1 and the specific surface area of the sample was 374 m^2/g.

CONCLUSIONS

The suggested procedure of precipitating magnesium silicate is an easy technique, non-time-consuming one and it yields products of interesting physicochemical parameters. The obtained results permit to conclude that precipitation temperature exerts no effect on contents of magnesium (in the form of MgO) and SiO_2. In every case the values have been very similar. Moreover, precipitation at any of the four tested temperatures have yielded exclusively amorphic silicate samples. Surface modification of synthetic magnesium silicates significantly affects their morphology and principal physicochemical parameters. Supplementation with U-311 silane has resulted in slight agglomeration of the studied silicate particles, which has been reflected by the respective particle size distribution. No such effects have been observed in magnesium silicate samples modified with Rokanol N3. Adsorptive properties of the studied unmodified silicates have not changed markedly following surface modification: the character of nitrogen adsorption/desorption isotherms has remained very similar. The only differences have been noted in values of BET specific surface area. In this case modification with either Rokanol N3 or U-311 silane has promoted decrease in the specific surface area. For the unmodified magnesium silicate (precipitated at 40˚C) BET area has amounted to 399 m^2/g, and for magnesium silicates modified with appropriate modifying agents it has ranged between 313 and 374 m^2/g.

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Ciesielczyk F., Krysztafkiewicz A., Jesionowski T., *Wpływ modyfikacji powierzchni na morfologię i parametry fizykochemiczne syntetycznego krzemianu magnezu,* Physicochemical Problems of Mineral Processing, 39 (2005) 155-164 (w jęz. ang).

Przedstawiono badania dotyczące modyfikacji powierzchni syntetycznych krzemianów magnezu. Krzemian magnezu otrzymano w reakcji strącania z użyciem roztworów siarczanu magnezu i metakrzemianu sodu. W trakcie prowadzonej syntezy do układu reakcyjnego wprowadzano czynniki modyfikujące powierzchnię syntetycznego krzemianu magnezu. Do tego celu wykorzystano odpowiednie ilości silanowych czynników proadhezyjnych oraz niejonowych związków powierzchniowo czynnych. Dla otrzymanych w ten sposób produktów wyznaczono parametry fizykochemiczne takie jak: gęstość nasypowa, chłonności wody (zwilżalność wodą), ftalanu dibutylu i oleju parafinowego, skład elementarny, średnice cząstek, powierzchnię właściwą oraz tendencję do sedymentacji.