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Filip CIESIELCZYK[*], Andrzej KRYSZTAFKIEWICZ[*], Teofil JESIONOWSKI[*]

ADSORPTIVE PROPERTIES OF SYNTHETIC MAGNESIUM SILICATES

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Studies were presented which were related to formation of a synthetic magnesium silicate in precipitation reaction employing solutions of sodium metasilicate and of appropriate inorganic magnesium salt. The studies aimed at obtaining precipitated products of best adsorptive properties. Both unmodified silicate and magnesium silicates modified with various agents were examined. Adsorptive properties were examined using determined nitrogen adsorption/desorption isotherms.

Key words: synthetic magnesium silicate, surface modification, adsorptive properties

INTRODUCTION

Application potential of the vast group of silicates and silicas to a significant extent reflects their physicochemical properties. The properties are determined, first of all, by parameters of the silicate formation process, including the applied reagents, their quantitative ratios and, possibly, supplementation with surface modifiers (Ciesielczyk 2004, 2005).

Due to the significant role of silicates (both natural and synthetic ones) as polymer fillers and selective adsorbents (Krysztafkiewicz 1996; Harris 2001), their surface activity involves an important problem. The activity is determined first of all by silanol groups (≡Si−OH) and their packing at the silicate surface (Jesionowski 2001). Synthetic magnesium silicates exhibit well developed surface and presence of reactive silanol groups and, thus, they can be included to the group of selective adsorbents.

The process of adsorption on their surface may also be intensified by surface modification of silicates using various agents. The most numerous group of modifiers involves silane coupling agents (Plueddeman 1991). Non-ionic surfactants and quaternary ammonium salts are also frequently used (Jesionowski 2001).

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[*] Poznan University of Technology, Institute of Chemical Technology and Engineering.
pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland, e-mail: Filip.Ciesielczyk@wp.pl

Introduction of a given modifier on the surface of a synthetic magnesium silicate results in the appearance of typical functional groups. The groups significantly affect efficiency of adsorption of various compounds on the silicate surface.

The very process of modification using, e.g., silane coupling agents provides an example of adsorption of the agents on the surface of a synthetic magnesium silicate. Literature of the subject contains mechanisms of silane adsorption on the surface of kaolin. Due to analogies in structure of kaolin, silicas and silicates the modifiers are expected to react in every case in line with the mechanisms (Johansson 1999, Azzopardi 1994).

Adsorptive properties of new products play a very important role in analysis of potential applications of synthetic magnesium silicates. It is assumed that the products may in future be used as selective and very effective adsorbents, particularly for cleaning sewages of heavy metals and the vast group of organic compounds. Therefore, in present study we undertook investigations on production of precipitated magnesium silicates of optimum adsorptive properties.

EXPERIMENTAL

MATERIALS

In the precipitation reaction an advantage was taken of 5% solutions of magnesium sulphate(VI), nitrate(V) and chloride (POCh S.A.), as well as of 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 modulus of 3.33 (VITROSILICON S.A.). The following modifying agents were used for surface modification of magnesium silicate: non-ionic surfactants produced by PCC ROKITA S.A. - oxyethylenated unsaturated fatty alcohols, Rokanol K3 and K7, of the general formula $RO(CH_2CH_2O)_nH$ $R=C_{16-22}$, where $n_{av}=3$ or $n_{av}=7$, respectively, and the produced by UniSil silane proadhesive compound, U-15 (*N*-2-aminoethyl-3-aminopropyltrimethoxysilane).

METHODS OF STUDIES

At the first stage of the studies magnesium silicate was precipitated using solutions of appropriate magnesium salt and sodium metasilicate. The reaction was conducted in a reactor of 500 cm^3 capacity, equipped with a rapidly top stirrer. The reactive system was placed in a thermostat.

The precipitation process was conducted either in the presence or in the absence of non-ionic surfactants (used to induce hydrophobic transformation of the surface). The obtained samples were additionally modified using U-15 aminosilane. The silane was deposited on their surfaces by „the dry technique”.

In order to determine magnesium silicate adsorptive properties their BET specific surface area, pore diameter and pore volumes were estimated using for the purpose nitrogen adsorption/desorption isotherms. The measurements were performed using ASAP 2010 apparatus (Micromeritics Instruments Co. USA).

RESULTS AND DISCUSSION

The nitrogen adsorption/desorption isotherms and pore size distribution of unmodified synthetic magnesium silicate obtained from $MgCl_2$ and on the surface of silicates precipitated in the presence of 5 wt./wt. of Rokanols K3 and K7 are presented in Fig.1 and Fig.2.

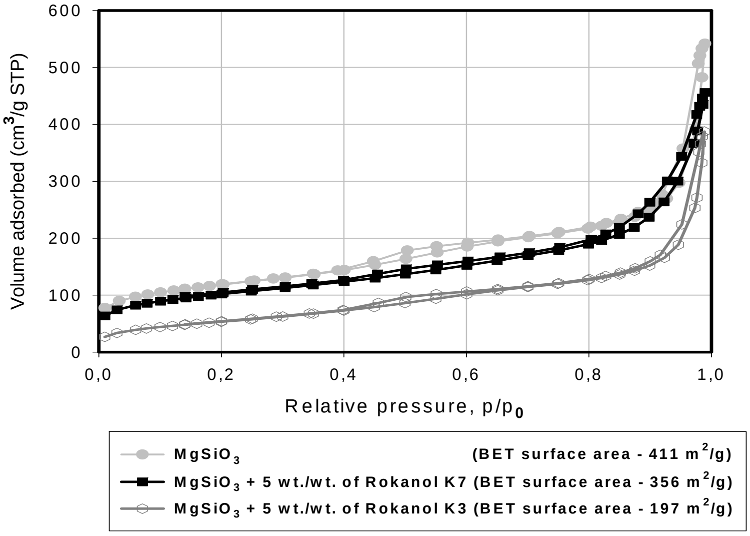

Fig.1. N_2 adsorption/desorption isotherms of the examined magnesium silicates precipitated from $MgCl_2$ solution

The shape of isotherms representing the modified samples resembled that of the isotherm obtained for the unmodified silicate sample. The amount of adsorbed nitrogen slightly increased until the relative pressure of 0.8 was obtained. At higher values of the relative pressure an abrupt increase was noted in the amount of adsorbed nitrogen. Such course of the isotherms pointed to high activity of the silicates. The adsorbed amount of nitrogen at p/p_o=1 reached the value of 543 cm^3/g for unmodified silicate, 457 cm^3/g for magnesium silicate precipitated in the presence of 5 wt./wt. of Rokanol K7 and 396 cm^3/g for magnesium silicate precipitated in the presence of 5 wt./wt. of Rokanol K3. The course of adsorption isotherms indicated that the magnesium silicates belonged to mesoporous sorbents (the amount of adsorbed nitrogen practically did not increase until the relative pressure reached the value of 0.7). On the other hand, significant differences were noted in the amount of adsorbed nitrogen and in values of BET specific surface area. For the unmodified silicate specific surface area amounted to 411 m^2/g while for the silicates precipitated in the presence of 5 wt./wt. of Rokanol K3 or K7 the surface amounted to 197 m^2/g and 356 m^2/g, respectively.

Comparison of pore size distribution (Fig.2) indicates that adsorptive forces linked to interaction with pore walls decrease with increasing pore size while molecular interactions introduce increasingly pronounced effects on the adsorption process. Various sizes of the individual pore groups reflect first of all their shape and properties of the adsorbent (Jaroniec 1999). In the case of mesopores their lower limit is sufficiently high to allow multilayered adsorption of adsorbate molecules.

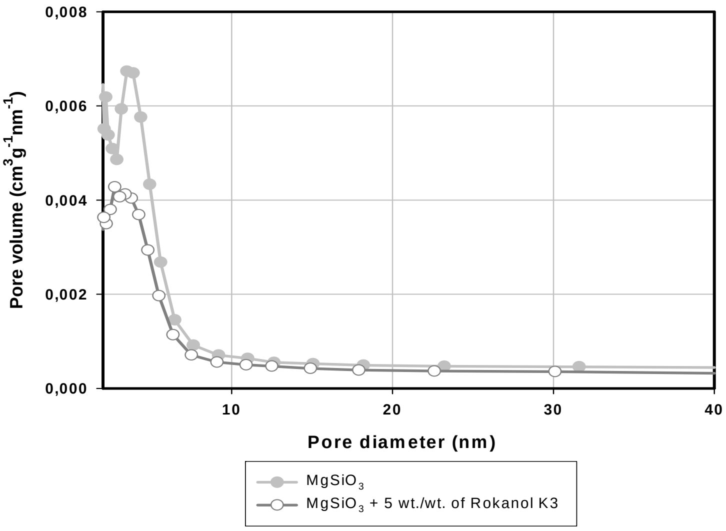

Fig. 2. Pore size distribution (BJH method) of the examined magnesium silicates precipitated from $MgCl_2$ solution

Nitrogen adsorption/desorption isotherms on the unmodified silicate precipitated from $Mg(NO_3)_2$ and for magnesium silicate precipitated in the presence of 5 wt./wt. of Rokanol K3 or K7 are presented in Fig. 3.

The character of isotherms was similar to those presented in Fig. 1. In the case of magnesium silicate precipitated from $Mg(NO_3)_2$ no significant differences were observed in the amounts of nitrogen adsorbed. For magnesium silicates subjected to no hydrophobization and those hydrophobically transformed using 5 wt./wt. of Rokanol K7 the amount was 592 cm^3/g, but for the magnesium silicate precipitated in the presence of 5 wt./wt. of Rokanol K3 maximum amount of adsorbed nitrogen reached 621 cm^3/g. In the case when magnesium nitrate(V) was used for precipitation of magnesium silicate the differences in specific surface area were no longer so extensive as those in the case of samples obtained from $MgCl_2$.

In the precipitation process of synthetic magnesium silicate solution of magnesium sulphate(VI) was also used. Isotherms obtained for silicate samples obtained using the substrate are presented in Fig. 4. In this case the lowest differences were observed in the maximum amounts of adsorbed nitrogen and in values of BET specific surface area. The curves manifested an identical character, pointing to mesoporous structure of the magnesium silicates. The amounts of adsorbed nitrogen ranged from 530 to 580 cm^3/g. Remarkably, specific surface area (estimated by BET technique) in cases of silicates precipitated in the presence of 5 wt./wt. of Rokanols K3 or K7 demonstrated higher values (433 cm^3/g and 453 cm^3/g, respectively) than that noted for the silicate precipitated in the absence of non-ionic surfactants (408 cm^3/g).

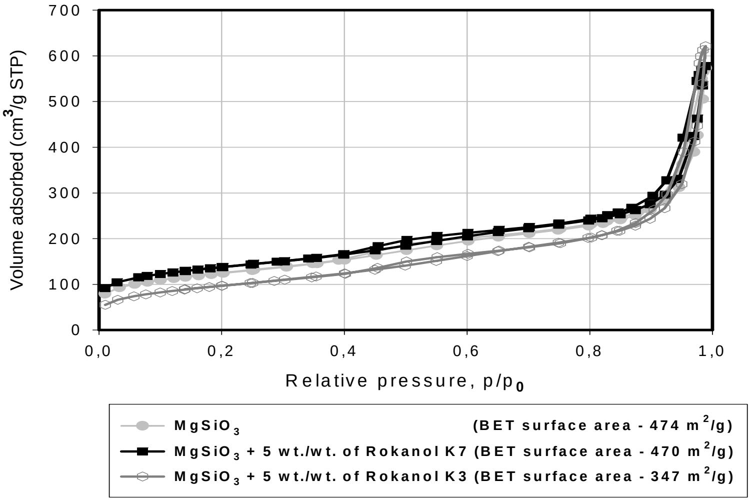

Fig. 3. N_2 adsorption/desorption isotherms of the examined magnesium silicates precipitated from $Mg(NO_3)_2$ solution

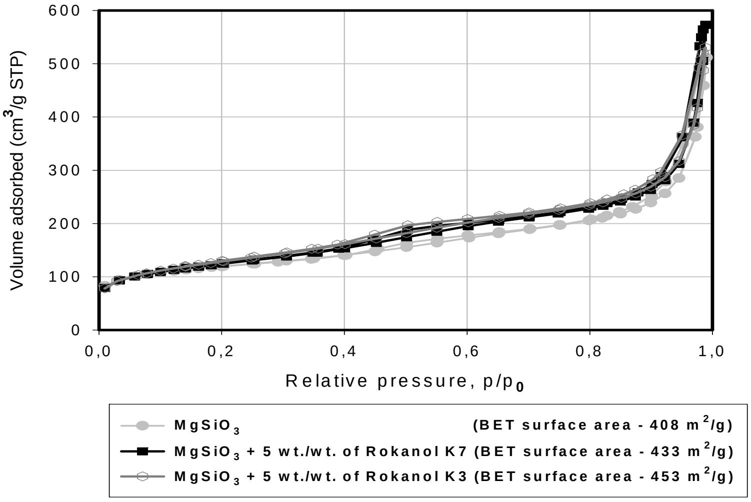

Fig. 4. N_2 adsorption/desorption isotherms of the examined magnesium silicates precipitated from $MgSO_4$ solution

Application of synthetic magnesium silicate as a selective adsorbent of heavy metals or organic compounds required searches for solutions which would promote the adsorption process. One of such solutions involved introduction to the synthetic magnesium silicate surface of typical functional groups which would freely react with the adsorbed agents. Such groups are contained, e.g., in silane coupling agents and their deposition to the surface of synthetic magnesium silicate was executed by ”the dry technique”. Nitrogen adsorption/desorption isotherms on the surface of magnesium silicates precipitated using magnesium sulphate(VI) in the presence or in the absence of 5 wt./wt. of Rokanol K3 and, in addition, modified by „the dry technique” with U-15 aminosilane are presented in Fig. 5.

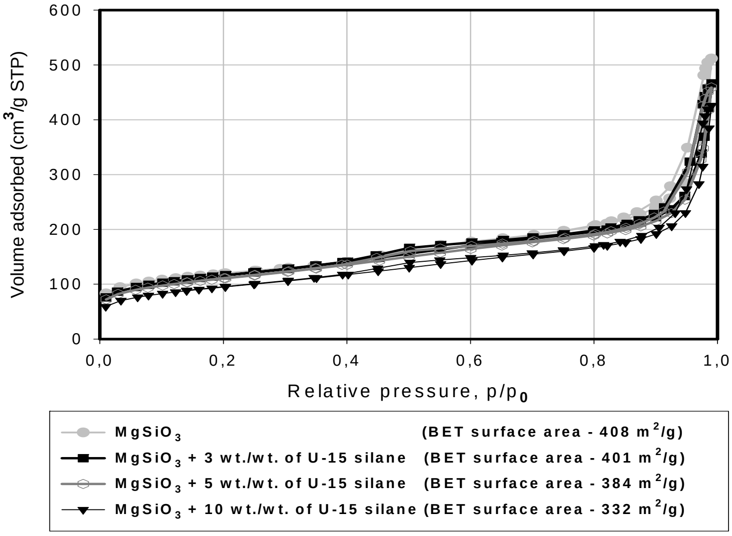

Fig.5. N_2 adsorption/desorption isotherms of the examined magnesium silicates precipitated from $MgSO_4$ solution modified with aminosilane U-15

Magnesium silicates precipitated in the absence of Rokanol K3 and modified with aminosilane (Fig. 5) manifested very similar course of isotherms of nitrogen adsorption/desorption. The amount of adsorbed nitrogen decreased with increasing amount of applied modifying agent. For the unmodified magnesium silicate the amount of adsorbed nitrogen was 509 cm^3/g, while for magnesium silicates modified using 3 or 5 wt./wt. of U-15 aminosilane they reached 477 cm^3/g and for magnesium silicate modified with 10 wt./wt. of the aminosilane it was 449 cm^3/g. Worth noting, similar tendencies were observed in the case of BET specific surface area. The unmodified magnesium silicate exhibited the highest BET specific surface area (408 m^2/g) and magnesium silicate modified with 10 wt./wt. of aminosilane manifested the lowest BET surface area (332 m^2/g). This might reflect the fact that binding to the surface of synthetic silicate the organo-functional silane occupied active centres and in this way decreased surface activity of the precipitated silicate. Additionally, the decreased specific surface area might be caused by steric hindrance produced by hydrocarbon chains of silicate surface adsorbed silanes, which in this way decreased nitrogen penetration to the silicate surface.

Similar relationships were observed in the case when magnesium silicate precipitated in presence of 5 wt./wt. of Rokanol K3 was subjected to aminosilane modification. Specific surface area decreased also with increasing amounts of the applied modifying agent. Again, the lowest BET specific surface area (332 m^2/g) was manifested by magnesium silicate modified with 10 wt./wt. of aminosilane.

Principal morphological and structural parameters of precipitated magnesium silicates determined by the nitrogen adsorption/desorption isotherms are listed in Table 1.

Table 1. Physicochemical parameters decided about adsorptive properties of unmodified and modified magnesium silicates

Precipitating agent	Amount of non-ionic surfactants	Modifying agent	Amount of modifying agent (wt./wt.)	Specific surface area BET (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
$MgCl_2$	-	-	-	411	0.80	5.5
	5 wt./wt. of Rokanol K3	-	-	197	0.67	6.3
	5 wt./wt. of Rokanol K7	-	-	356	0.61	7.9
$Mg(NO_3)_2$	-	-	-	474	0.83	5.5
	5 wt./wt. of Rokanol K3	-	-	347	0.87	6.2
	5 wt./wt. of Rokanol K7	-	-	470	0.98	7.3
$MgSO_4$	-	-	-	408	0.73	5.5
	5 wt./wt. of Rokanol K3	-	-	433	0.85	5.6
	5 wt./wt. of Rokanol K7	-	-	453	0.79	5.2
$MgSO_4$	-	U-15 silane	3	401	0.68	5.2
	-		5	384	0.67	5.2
	-		10	332	0.63	5.2
$MgSO_4$	-	U-15 silane	3	384	0.64	4.8
	5 wt./wt. of Rokanol K3		5	376	0.64	4.9
	5 wt./wt. of Rokanol K3		10	364	0.67	4.8

Among the unmodified samples, the highest specific surface area (474 m^2/g) was shown by magnesium silicate obtained from $Mg(NO_3)_2$ and the lowest one by the silicate obtained from $MgSO_4$. As compared to unmodified samples, samples precipitated in the presence of non-ionic surfactants showed higher value of specific surface area only in the case of magnesium silicate precipitated from $MgSO_4$.

Neither the original substrates nor the applied modifying agents significantly affected the remaining adsorptive parameters of precipitated silicates. In all the cases pore volumes and pore diameters demonstrated similar values.

CONCLUSIONS

Formation of synthetic magnesium silicates by precipitation from sodium metasilicate solutions and solutions of various inorganic magnesium salts represents an interesting approach, which yields active, highly dispersed adsorbents and fillers. The precipitated in this way silicates manifest a relatively high value of BET specific surface area, which indirectly points to their high surface activity. The highest values of specific surface area have been shown by magnesium silicate samples obtained from $MgSO_4$ (408-453 m^2/g) or from $Mg(NO_3)_2$ (470-474 m^2/g). Among the three various magnesium salts, magnesium chloride used for magnesium silicate precipitation has proven to be least advantageous. Precipitation of magnesium silicate in the presence of 5 wt./wt. of Rokanols K3 or K7 has resulted in a radically decreased specific surface area, even to 197 m^2/g for the silicate precipitated from $MgCl_2$ in the presence of 5 wt./wt. of Rokanol K3. The situation has been analogous when the surface of synthetic magnesium silicate has been modified using silane coupling agent. Similarly to the effects of non-ionic surfactants, the modification has resulted in marked decrease in specific surface area of precipitated silicates. It is worth stressing that neither the employed substrates nor modifying agents have clearly affected the remaining adsorptive parameters (pore volume and pore diameter).

Summing up, the obtained synthetic magnesium silicates of a relatively high surface activity may find application as selective adsorbents of heavy metals and of selected organic compounds.

ACKNOWLEDGEMENTS

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REFERENCES

AZZOPARDI M.J., ARRIBART H., 1994, *In situ FTIR study of the formation of an organosilane layer at the silica/solution interface*, Journal of Adhesion, 46, 103-115.

CIESIELCZYK F., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2004, *Influence of precipitation parameters on physicochemical properties of magnesium silicates*, Physicochemical Problems of Mineral Processing, 38, 197-205.

CIESIELCZYK F., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2005, *Influence of surface modification on morphology and physicochemical parameters of synthetic magnesium silicate*, Physicochemical Problems of Mineral Processing, 39, 155-164.

HARRIS R.G., WELLS J.D., JOHNSON B.B., 2001, *Selective adsorption of dyes and other organic molecules to kaolinite and oxide surfaces*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 180, 131-140.

JARONIEC M., KRUK M., OLIVIER J.P., 1999, *Standard nitrogen adsorption data for characterization of nanoporous silicas,* Langmuir 15 (16), 5410-5413.

JESIONOWSKI T., KRYSZTAFKIEWICZ A., 2001, *Influence of silane coupling agents on surface properties of precipitated silicas*, Applied Surface Science, 172, 18-32.

JESIONOWSKI T., KRYSZTAFKIEWICZ A., SKRZYPCZAK A., 2001, *Effects of quartenary ammonium chlorides on the surface properties of precipitated silicas,* Tenside Surfactants and Detergents, 38,158-163.

JOHANSSON U., HOLMGREN A., FORSLING W., FROST R.L., 1999, *Adsorption of silane coupling agents onto kaolinite surface*, Clay Minerals, 34, 239-246.

KRYSZTAFKIEWICZ A., RAGER B., MAIK M., WALKOWIAK J., 1996, *Modified sodium aluminium silicate – a highly dispersed polymer filler and pigment*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 113, 203-214.

PLUEDDEMAN E.P., 1991, *Silane coupling agents*, 2nd Edition Plenum Press, New York.

Ciesielczyk F., Krysztafkiewicz A., Jesionowski T., *Właściwości adsorpcyjne syntetycznych krzemianów magnezu,* Physicochemical Problems of Mineral Processing, 41 (2007) 185-193 (w jęz. ang.).

Przedstawiono badania dotyczące otrzymywania syntetycznego krzemianu magnezu w reakcji strącania z wykorzystaniem roztworów metakrzemianu sodu oraz odpowiedniej nieorganicznej soli magnezu. Badania zostały ukierunkowane w stronę uzyskania jak najlepszych właściwości adsorpcyjnych strącanych produktów. Przebadano zarówno krzemian niemodyfikowany jak i krzemiany magnezu modyfikowane różnymi czynnikami. Właściwości adsorpcyjne analizowano na podstawie wyznaczonych izoterm adsorpcji/desorpcji azotu na powierzchni syntetycznych krzemianów.