Oil absorption in mesoporous silica particles

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Abstract

Mesoporous silica particles were prepared from highly basic sodium silicate solutions, having different silica modulus and SiO_2 concentrations, by adding sulphuric acid at different temperatures. Pore structure of prepared silica particles (aggregates) is strongly influenced by processing conditions and easy controllable in broad range of the specific surface area, pore size, pore volume and size distribution. It is shown that there is a clear correlation between volume of absorbed oil and processing parameters used in preparation of silica aggregates. Thus, oil absorption is higher in the samples prepared from sodium silicate solution with higher SiO_2 concentration and at higher synthesis temperature.

Keywords*: mesoporous, silica, synthesis, oil absorption*

I. Introduction

Already in 1956 Kolbe [1] reported the synthesis of porous, monodispersed silica particles based on the hydrolysis and subsequent condensation of silica alkoxides in ethanol. Later Stöber *et al.* [2] exploited the experimental conditions of this reaction systematically and developed now well known Stöber process. After that numerous synthesis routes and different precursors have been used for preparation of silica particles. Thus, silicon tetrachloride and sodium silicate solution were extensively investigated for preparation of dense and porous silica and their application in industry [3,4].

Mesoporous silica particles, material with high surface area and pore sizes in the range of 2–50 nm, possess high surface free energy and they have attracted much attention for numerous applications in adsorption, separation, catalysis and drug delivery. Different mechanisms for the formation of mesoporous silica particles were suggested, but the aggregation growth model [5,6] is broadly accepted. This model states that particle growth occurs due to an aggregation of primary particles which are nucleated in a supersaturated solution, producing a porous structure. However, pores could be closed during aging in the solution due to the dissolution/reprecipitation process. Thus, depending on the synthesis parameters, the structure of prepared silica particles may vary from isolated dense particles to porous agglomerates with different pore size and shape, pore size distribution and pore volume.

The aim of this work is to synthesize mesoporous silica particles from sodium silicate solution and investigate their capability in oil absorption.

II. Experimental

Mesoporous silica particles were prepared from highly basic sodium silicate solutions (Water glass, Alumina Factory-Birač, Zvornik), having three different silica modulus (SiO_2/Na_2O molar ratio - low, l = 2.5, medium, m = 2.8 and high, h = 3.5) and concentrations of SiO_2 (low, l = 0.6 mol/l, medium, m = 0.9 mol/l and high, h = 1.3 mol/l). The synthesized powders have notation S_{xy}-T, where T is synthesis temperature, x describes silicate modulus ($x = l$, m or h) and y describes SiO_2 concentration ($y = l$, m or h). Sulphuric acid (H_2SO_4 = 3.7 mol/l) was slowly added into a well stirred sodium silicate solutions at three different temperatures 50, 70 and 90°C to precipitate silica particles. Finally, pH was adjusted at value of ~4 to prevent dissolution process. The white precipitated powders were washed with distilled water, separated from liquid phase by filtration and finally dried at 120°C for 1 day.

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The specific surface area (according to the BET method), average pore size, pore volume and pore size distribution (according to the BJH model) of as-synthesized powders were measured by low temperature nitrogen adsorption using a Quantachrom Autosorb-3B instrument. Powder XRD patterns were obtained by Philips PW difractometer 1729, using CuKα radiation at 40 kV and 50 mA, in 2θ = 5–60° and step size of 0.02°. Particle size and size distribution of as-synthesized silica powders were measured by light scattering (Microsizer 201C, VA Instruments, Sank-Petersburg, Russia) and ZetaSizer Nano-ZS, Malvern instruments, Great Britain). Size and morphology of particles were examined using a scanning electron microscope (SEM JEOL, 6460LV, operating at 20 kV).

The oil absorption was determined according to the method MA.TS.02 used as a standard test in industry. Dibutylphthalate was slowly added (0.2 ml/min) to 1 g of dry powder up to the point at which the compacted mass was formed and no dibutylphthalate trace can be seen on the plate. The measured dibutylphthalate volume (per gram of investigated sample) was recorded and expressed as the oil absorption of the investigated powder sample. Similar method was used by Zhou *et al.* [7] and showed good reproducibility.

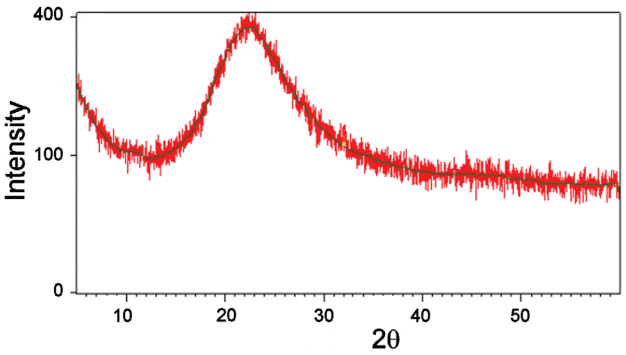


Figure 1. XRD of as-synthesized silica powder

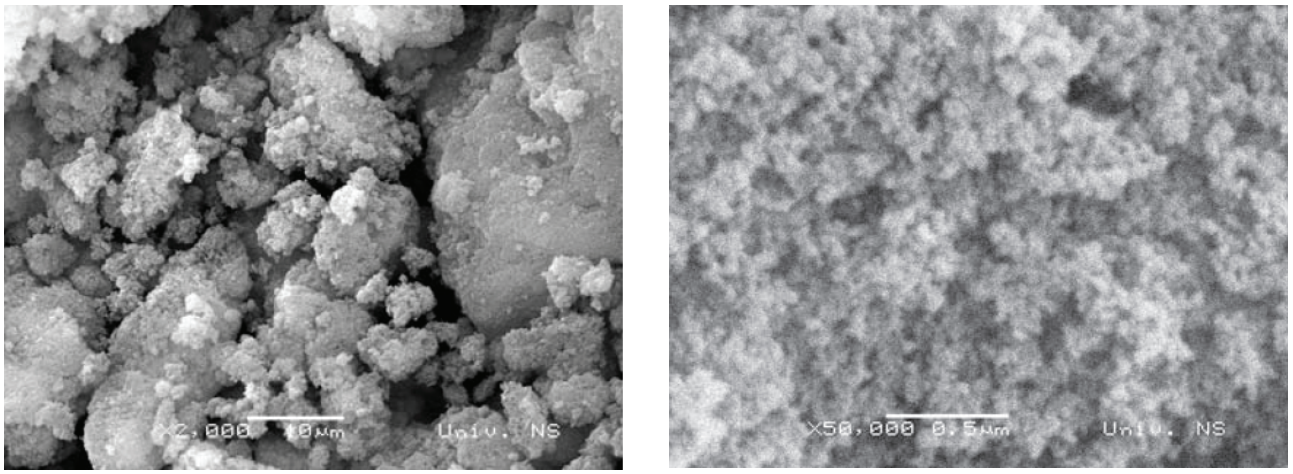
III. Results and discussion

All silica particles, synthesized from sodium silicate solution, are amorphous (Fig. 1) and consist of aggregates having size from ~1 μm to few tenths of microns (Fig. 2a). They are formed by aggregation of primary particles, which are nucleated in a supersaturated solution, producing a porous structure. Small primary particles (and pores between them) can be clearly distinguished on SEM micrographs (Fig. 2b). It is shown [8] that the pore structure of prepared silica particles (aggregates) is strongly influenced by processing conditions and easy controllable in broad range of the specific surface area, pore size, pore volume and size distribution. The obtained mesoporous silica powders with high total pore volume have high potential for application in oil absorption.

Oil absorption in the silica particles synthesized from sodium silicate solution with different silica concentration depending on silica modulus is presented in Fig. 3. It can be seen that silica powders synthesized at different conditions have very large difference in oil absorption. Thus, the silica powders S_{hl}-50, S_{hl}-70 and S_{hl}-90, prepared from sodium silicate solution with high silica modulus, SiO_2/Na_2O = 3.5, and low SiO_2 concentration, can absorb ~1 ml/g. Oil absorption in the silica powders S_{ml}-50 and S_{ll}-50, prepared from sodium silicate solution with medium and low silica modulus (SiO_2/Na_2O = 2.8 and 2.5) and low SiO_2 concentration at 50°C, is only 0.8 and 0.65 ml/g, respectively. However, oil absorption in the powders S_{hh}-90, synthesized from sodium silicate solution with the highest concentration of SiO_2 (1.6 mol/l) at 90°C, is even > 3.5 ml/g.

It is obvious that there is clear correlation between volume of absorbed oil and processing parameters used in preparation of silica aggregates. Thus, oil absorption is higher in the samples prepared at higher SiO_2 concentration and temperature, only discrepancy can be seen for the sample S_{lh}-90 (Fig. 3c).

To understand this behaviour it is necessary to cor-



a) **b)**

Figure 2. SEM micrographs of S_{lh}-90 powder at: a) low and b) high magnification

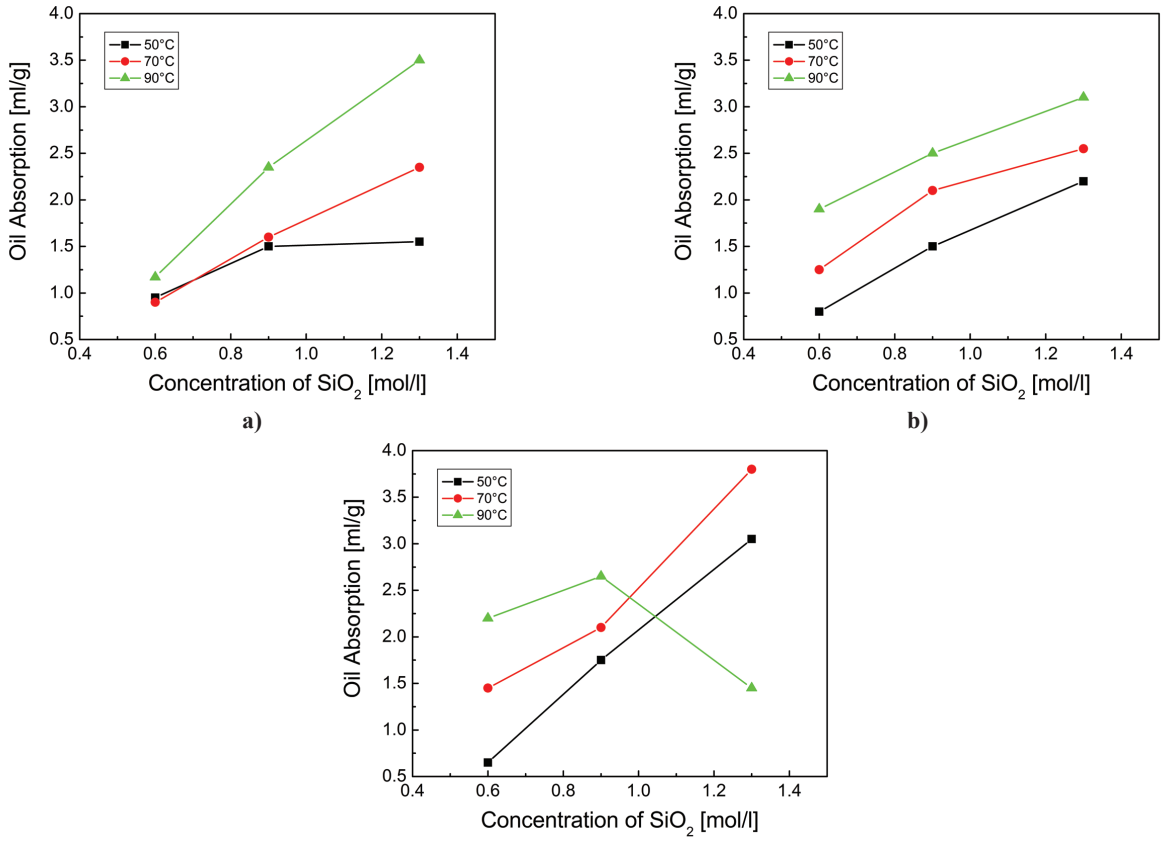


Figure 3. Oil absorption in silica powders synthesized from sodium silicate solutions with different silica concentration: a) high, b) medium and c) low silica modulus

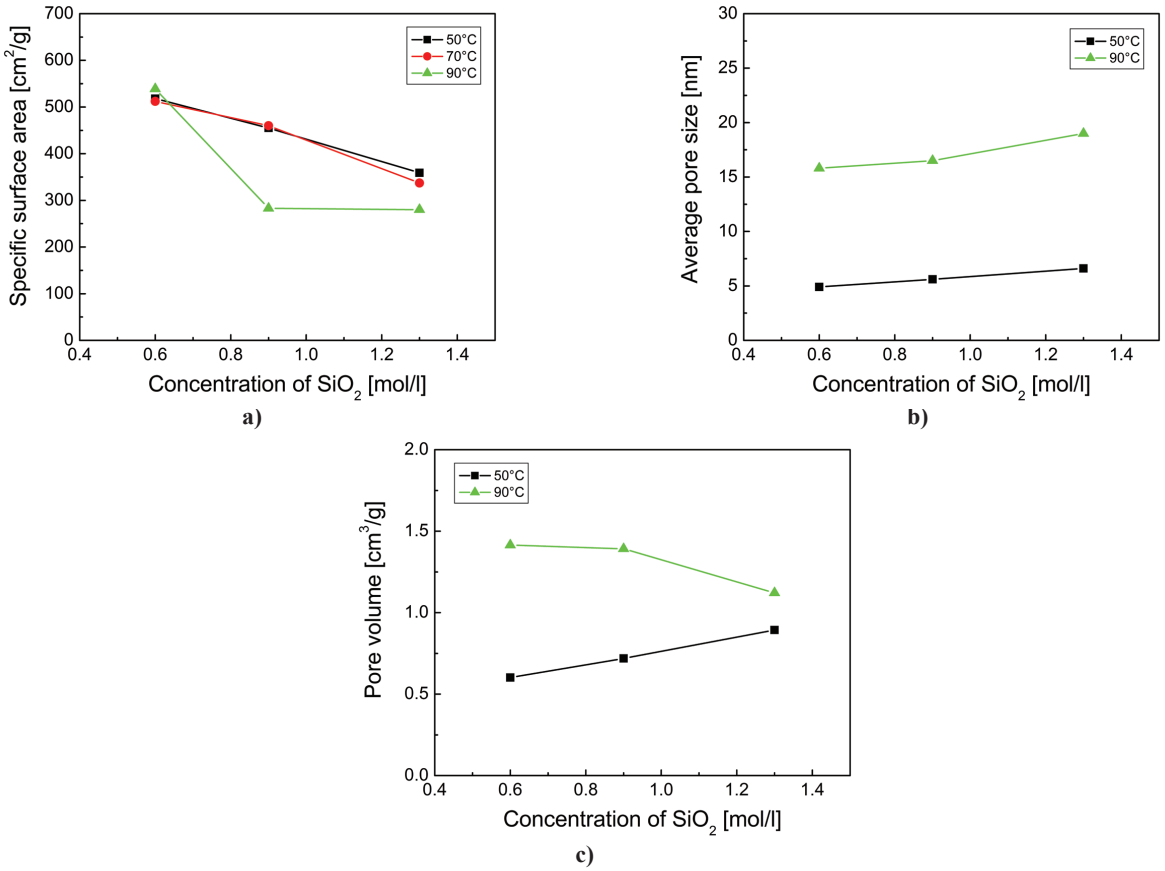


Figure 4. Specific surface area (a), average pore size (b) and pore volume (c) of silica powders synthesized from sodium silicate solutions with different silica concentration and high silica modulus

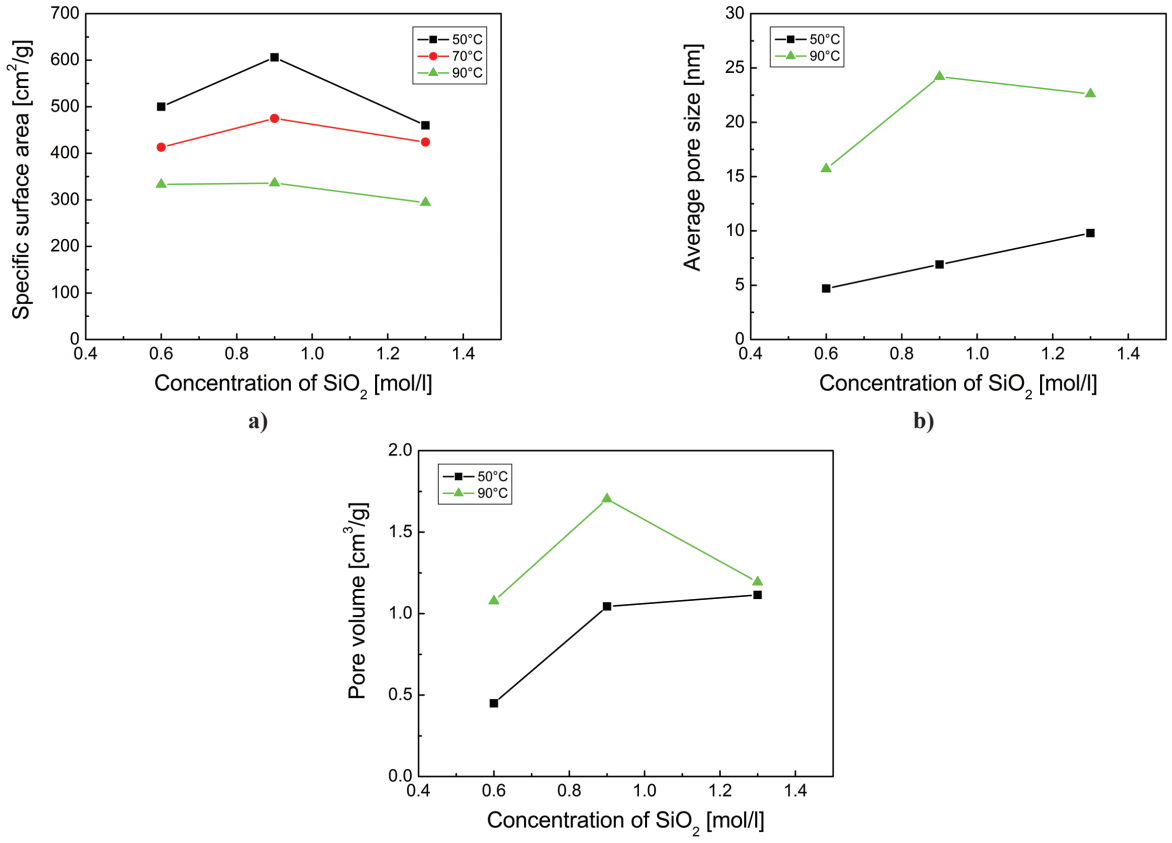


Figure 5. Specific surface area (a), average pore size (b) and pore volume (c) of silica powders synthesized from sodium silicate solutions with different silica concentration and medium silica modulus

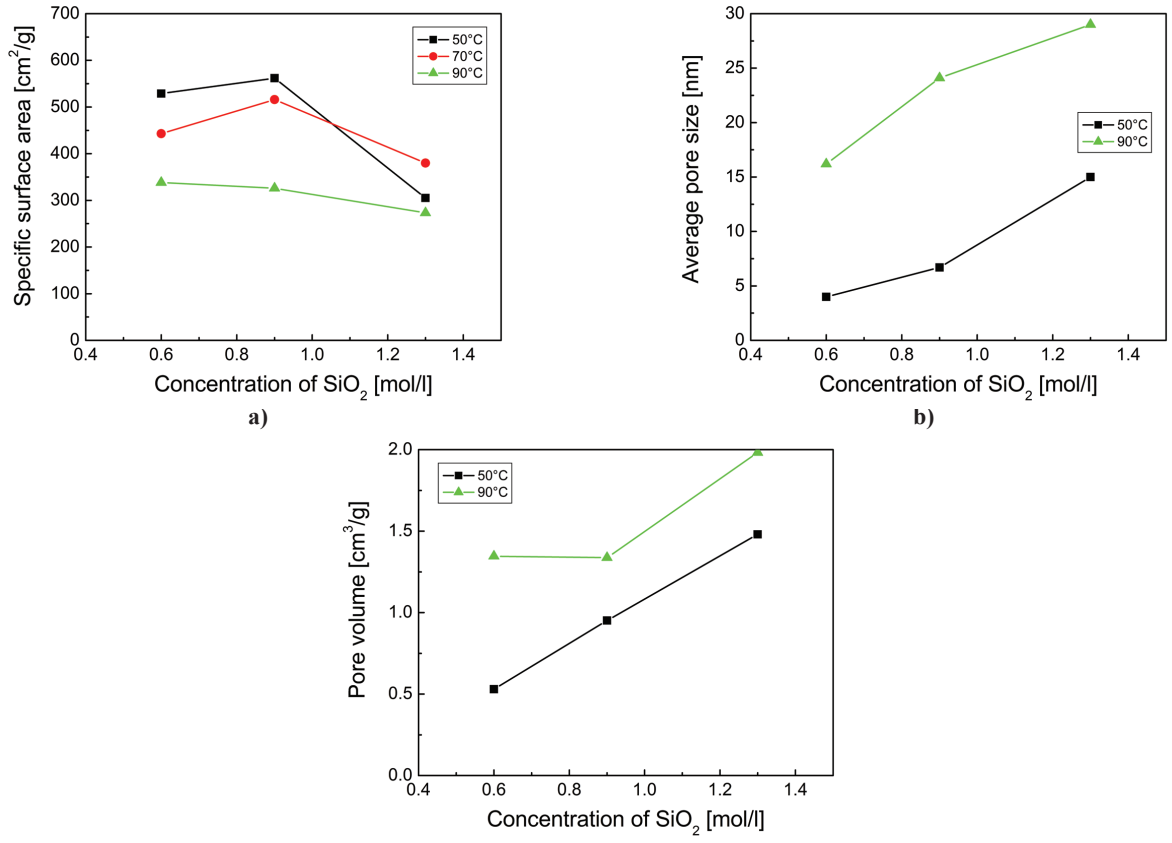


Figure 6. Specific surface area (a), average pore size (b) and pore volume (c) of silica powders synthesized from sodium silicate solutions with different silica concentration and low silica modulus

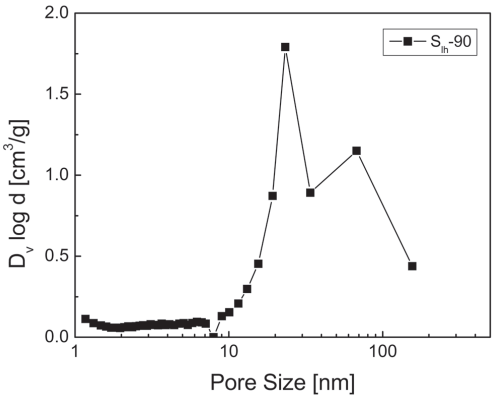


Figure 7. Pore size distribution of silica powder S_{lh}-90

relate powder characteristics (given in Figs. 4–6) with oil absorption data. It can be concluded that lower oil absorption is characteristic of the powders with higher surface area, smaller average pore size and lower pore volume. Thus, the lower oil absorption has the silica powders S_{hl}-50, S_{ml}-50 and S_{ll}-50 (prepared from sodium silicate solution with lower SiO_2 concentration at 50°C) with high specific surface (518, 500 and 529, respectively), small average pore size (4.9, 4.7 and 4.0 nm, respectively) and low pore volume (0.601, 0.449 and 0.530 ml/g, respectively). On the other hand, the higher oil absorption have the silica powders S_{hh}-90, S_{mh}-90 and S_{lh}-70 with low specific surface area (280, 294 and 380, respectively), large average pore size (19.0, 22.6 and 24.0 nm, respectively) and high pore volume (1.121, 1.193 and 1.501 ml/g, respectively). According to this logic someone can conclude that the higher oil absorption can be expected in the powder S_{lh}-90, as it has the higher pore volume of 1.982 ml/g, large average pore size of 29.0 nm and small specific surface area of 273 m^2/g. However, the oil absorption in the sample S_{lh}-90 is very low. We believe that the main reason is very large average pore size and existence of high portion of pores >20 nm (Fig. 7), which can only be partially filled with dibutylphthalate (contrary to the samples with smaller pores which can be fully filled with oil).

IV. Conclusions

Mesoporous silica particles were prepared from highly basic sodium silicate solutions, having different silica modulus and SiO_2 concentrations, by adding sulphuric acid at different temperatures. Pore structure of prepared silica particles (aggregates) is strongly influenced by processing conditions and easy controllable in broad range of the specific surface area, pore size, pore volume and size distribution.

Silica powders synthesized at different conditions have very large difference in oil absorption. It is shown that there is clear correlation between volume of absorbed oil and processing parameters used in preparation of silica aggregates. Thus, oil absorption is higher in samples prepared from sodium silicate solution with higher SiO_2 concentration and at higher synthesis temperature. Thus, the silica powders prepared from sodium silicate solution with high silica modulus and low SiO_2 concentration can absorb ~1 ml/g. Oil absorption in the silica powders prepared from sodium silicate solution with medium and small silica modulus and low SiO_2 concentration at 50°C, is only 0.65 ml/g. However, oil absorption in the powders synthesized from sodium silicate solution with the highest concentration of SiO_2 at 90°C is even > 3.5 ml/g.

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