

Redispersion of dried colloidal silica

Investigating the redispersibility of dried surface-modified colloidal silica in solvents of different polarity

Master's thesis in Materials chemistry

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Gothenburg, Sweden 2019

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Cover:

An illustration of the two different silane modifications of colloidal silica and the three isocyanate surface modifications of the dried silica powder

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Abstract

Colloidal silica is an aqueous dispersion of discrete silica particles and has a broad applicability; however, as these silica sols are water borne it limits the applications. Hence, using surface modification of colloidal silica as a tool to prevent aggregation upon drying and allowing redispersion in solvents with different polarity through further surface-modification of the dried particles is of great interest.

The aim of this thesis project was to investigate the redispersibility of two differently surface modified, dried, hydrophilic silica particles in solvents with varying polarity. One was modified with 3-glycidoxypropyltriethoxy silane, while the other had a coverage composed of both 3-glycidoxypropyltriethoxy and 3-aminopropyltriethoxy silane. Three different routes of redispersion were examined: redispersion without additives, redispersion using dispersants and redispersion through further surface modification.

This study shows that it is possible to redisperse the different silica powders in water and regain the original particle size. Redispersion of silica was only possible in water and ethylene glycol. Presence of free extra salt in the dried powder appeared to promote redispersibility and reduced the energy input required for redispersion. Smaller agglomerate size of the dried powder played a significant role in promoting redispersion of the diol modified powder. This was, however, not observed for the diol- and amine modified surface, suggesting that surface modification plays an important role in redispersion as well.

In organic solvent, the overall hydrophilic character of the dried powders prevented efficient redispersion. A clear difference in surface-dispersant interaction depending on surface modification of the silica was observed. Adding dispersants improved the dispersibility of the combined 3-glycidoxypropyltriethoxy silane and 3-aminopropyltriethoxy silane surface-modified silica. However, large amounts of sedimentation were still present.

The third approach, for which further covalent surface-modification of the pendant hydroxyl groups in the surface-modified colloidal silica was done with isocyanates, showed a real improvement of particle-solvent interactions. No sample fully redispersed, however, a higher molecular weight of the ligand seems beneficial for redispersion. Furthermore, ligand solvent interactions, such as π - π bonding, appear to improve redispersibility as well, since the turbid phase contained a higher silica percentage compared to samples where pi-pi bonding was not present.

A universal method for redispersion of surface modified colloidal silica using dispersants was not found, and these results indicates that surface modification of the colloidal silica, dispersant and solvent all must be considered and chosen to achieve efficient dispersion. Further modification of the particle surface of the dried silica powder proved to be most fruitful for redispersion attempts in organic solvent, but additional investigations of reaction conditions need to be performed as none of the samples fully redispersed.

Keywords: *Colloidal silica, Nanoparticles, Surface modification, Redispersion, Solvents, Dispersants, Isocyanates*

Table of content

1. INTRODUCTION	1
1.1 AIM	1
1.2 LIMITATIONS.....	1
1.3 SPECIFIC ISSUES TO BE ADDRESSED DURING THE INVESTIGATION.	2
2. THEORY.....	3
2.1 COLLOIDAL SILICA	3
2.1.1 <i>Stability</i>	3
2.2 DRYING COLLOIDAL SILICA.....	4
2.3 DISPERSING HYDROPHILIC SILICA PARTICLES.....	5
2.3.1 <i>In aqueous media</i>	5
2.3.2 <i>In non-aqueous media</i>	5
2.4 CHARACTERIZATION TECHNIQUES.....	7
2.4.1 <i>Scanning electron microscope</i>	7
2.4.2 <i>Dynamic light scattering</i>	7
2.4.3 <i>Thermogravimetric analysis</i>	8
2.4.4 <i>Fourier transform infrared spectroscopy</i>	8
3. MATERIALS AND METHODS	9
3.1 CHEMICALS	9
3.2 SILICA NANOPARTICLES SURFACE MODIFICATION	10
3.2.1 <i>CC-silane modification</i>	10
3.1.2 <i>CCA-silane modification</i>	10
3.1.3 <i>Ion exchange</i>	10
3.2 POWDER PRODUCTION	10
3.2.1 <i>Drying</i>	11
3.2.2 <i>Ball milling</i>	11
3.3 REDISPERSION WITHOUT ADDITIVES.....	11
3.4 REDISPERSION USING ADDITIVES	12
3.4.1 <i>Adding dispersant prior to drying</i>	14
3.5 SURFACE MODIFICATION WITH ISOCYANATES.....	14
3.5.1 <i>Effect of bound water</i>	14
3.5.2 <i>Effect of reaction conditions</i>	15
3.5.3 <i>Effect of solvent</i>	16
3.6 CHARACTERIZATION TECHNIQUES.....	16
3.6.1 <i>SEM</i>	16
3.6.2 <i>TGA</i>	16
3.6.3 <i>DLS</i>	17
3.6.4 <i>FTIR</i>	17
4. RESULTS AND DISCUSSION.....	18
4.1 SOL PRODUCTION	18
4.2 POWDER PRODUCTION	18
4.2.1 <i>Effect of drying method</i>	18
4.2.2 <i>Ball milling</i>	19
4.3 REDISPERSION WITHOUT ADDITIVES.....	20
4.3.1 <i>Redispersion in water</i>	20
4.3.2 <i>Redispersion in ethylene glycol</i>	23
4.4 REDISPERSION USING ADDITIVES	25
4.4.1 <i>Redispersion of silica with diol-covered surface</i>	25
4.4.2 <i>Redispersion of Silica with both amine- and diol-covered surface</i>	27
4.5.3 <i>Adding dispersant prior to drying</i>	28
4.5 SURFACE MODIFICATION	29
4.5.1 <i>Effect of bound water</i>	29

4.5.2 <i>Surface modification in Toluene</i>	30
4.5.3 <i>Other solvents</i>	32
4.6 GENERAL DISCUSSION.....	34
5. CONCLUSION	36
6. FUTURE WORK	36
7. REFERENCES	37
APPENDIX	I

1. Introduction

Colloidal silica is a dispersion of amorphous, nonporous silica nanoparticles [1], that are used in many different applications for instance as flocculants in papermaking, in polishing slurries for the electronics industry, as supporting material for catalysts and as additives in paints and coatings. [2] Industrially, colloidal silica is produced as waterborne dispersions. These silica particles form irreversible aggregates as water is removed. Hence, it is of great interest to develop strategies that allow colloidal silica to redisperse and regain its initial size. Furthermore, it is beneficial if such colloidal silica can be redispersed in organic solvent, as it would further broaden the applicability.

As previously mentioned, drying colloidal silica results in non-redispersible aggregates due to the formation of siloxane bonds between particles. However, the aggregate formation may be avoided by e.g. steric stabilization of the nanoparticles. One way of achieving this is by the derivatization of the silica nanoparticle surface with silanes, physically hindering siloxane bond formation. Upon drying, these silane-modified colloidal silicas tend to form agglomerates. Agglomerate formation is reversible due to the weak physical interactions between the particles, making redispersion possible.

Silane surface modification of colloidal silica can yield both polar and nonpolar particles depending on the silane used. In this project, hydrophilic silanes have been used, generating polar particles redispersible in aqueous solutions. However, in organic nonpolar environments, the silane modified colloidal silica will not be redispersible as the functional groups of the silane will be hydrophilic and therefore not be compatible with the solvent. Hence, the physical bonds in the agglomerates will not break and the particles will not regain their original particle size. To break these physical bonds, different redispersion approaches can be examined.

One approach to redisperse colloidal silica in organic solvents is to break the agglomerates by introducing dispersants compatible with the solvent and that have an affinity to bind to the particle surface, either to the solvent upon redispersion or to the aqueous sol before drying. An alternative route is further covalent modification of the dried particles with hydrophobic groups. A range of different chemicals are suitable for this and the choice is generally dependent on the application and the dispersion media.

For this master thesis, the focus was to investigate the redispersibility of silane modified colloidal silica in solvents of different polarity. The problem was tackled by exploring three different routes to enhance the redispersion. The first route meant redispersing silica powder by using heat and sonication, in the second approach the use of dispersants was examined on whether they enhanced the redispersibility or not and the third route involved further surface-modification of the particle surface with hydrophobic surface modifiers during redispersion.

1.1 Aim

The aim of this master's thesis was to investigate the redispersibility of silane modified colloidal silica. There are three main routes of redispersion to be explored: redispersion through heat and sonication, addition of dispersants and by surface modification using isocyanates. The desired outcome is to regain the original size of the colloidal silica particles after redispersion.

1.2 Limitations

- This project only focused on silica nanoparticles with two different surface modifications, namely 5 μmol 3-glycidoxypropyltriethoxy silane surface modification and 4.5 μmol 3-glycidoxypropyltriethoxy silane + 0.5 μmol 3-aminopropyltriethoxy silane surface modification.
- All silica sols were dried using rotary evaporation followed by an additional drying step at 110 °C in an oven overnight. The spray-dried silica used was obtained from Nouryon.
- Nine solvents of different polarity were chosen to investigate redispersibility in solvents of varying polarity.

- Nine different dispersants were chosen due to their difference in size and surface-active groups. All dispersants are commonly used in industrial settings.
- Phenyl isocyanate, cyclohexyl isocyanate and octadecyl isocyanate were chosen as representative isocyanates for further surface-modification as they can react with surface diol groups.
- Experiments were performed using heat, stirring and sonication. No other types of treatment were explored.

1.3 Specific issues to be addressed during the investigation.

- Can dried colloidal silica be fully redispersed in solvents, regaining the original size, by using only heat and sonication?
- Does addition of dispersant to the solvent help redispersion?
- Does addition of small amounts of dispersants/surfactants before drying help redispersion?
- Does further surface modification with isocyanates help in regaining the nanosize of the colloidal silica upon redispersion?

2. Theory

2.1 Colloidal silica

Colloidal silica are stable dispersions of amorphous silica nanoparticles. These dispersions are mainly waterborne and commonly referred to as silica sols. [3] Colloidal silica is naturally occurring in nature and is formed during a high-temperature and high-pressure reaction where water is saturated with quartz. Industrially, colloidal silica is commonly produced through various processes using sodium silicate solutions. In order to obtain a stable sol, it is required to keep the produced silica particles under alkaline conditions while they grow to a specific size. The particles are kept negatively charged to avoid gel formation or flocculation. [3] In this study, Levasil colloidal silica obtained from Nouryon was used.

The silica surface consists of silanol groups and silicon atoms bound through siloxane bonds. [4] The charge of these silanol groups is dependent on the pH. The isoelectric point, the pH at which a certain molecule is electrically neutral, is approximately pH 2 for silica. [3] Hence, silica particles are positively charged at a pH below 2 and negatively charged at higher pH. The silica surface at pH 2 is illustrated in Figure 1 below.

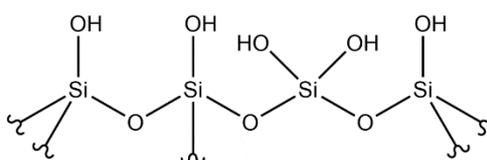


Figure 1. Fully hydroxylated silica surface in water at pH 2.

As illustrated above, the silica particle surface is hydroxylated and for fully hydroxylated surfaces, a total of $8 \mu\text{mol}$ hydroxyl groups per m^2 is available at the surface [5]. These silanols can be further modified with organosilanes to modify the properties of the particles. [3]

2.1.1 Stability

Colloidal silica needs to be stabilized to prevent particle aggregation. Particles in liquid dispersions can be stabilized by either electrostatic repulsion or by a protective layer of adsorbed molecules at the surface. These ways of stabilizing a dispersion are called electrostatic and steric stabilization, where steric stabilization works both in solution and in dried state. Figure 2 illustrate steric and electrostatic stabilization, which can also be combined to yield a mechanism that is called electrosteric stabilization. [1]

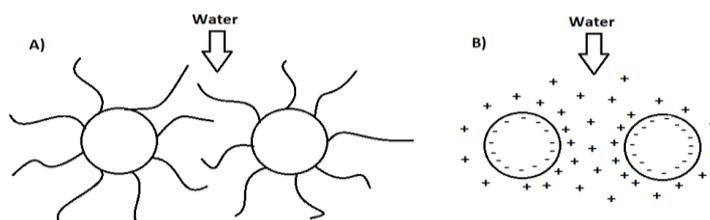


Figure 2. A) Steric stabilization in an aqueous system. B) Electrostatic stabilization in an aqueous system.

When two sterically stabilized silica particles come close, their respective stabilization layer overlap, the conformational entropy is decreased. The decreased entropy increases Gibbs energy, meaning that it will be unfavorable for two silica particles to come further into proximity. This leads to an entropic repulsion, keeping the two silica particles separated. [1] Hence, steric stabilization of silica particles prevents the

formation of covalent inter-particle siloxane bonds from forming. [3] Figure 3 illustrates these covalent siloxane bonds.

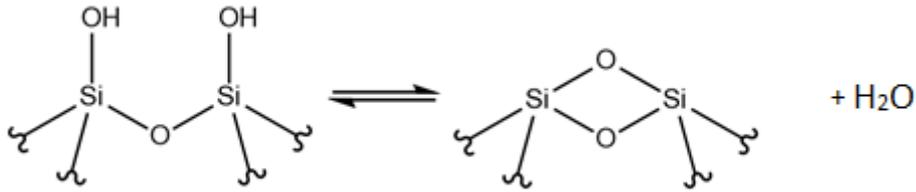


Figure 3. Equilibrium of siloxane bond formation.

The siloxane bond formation in a dispersion is dependent on the size of the dispersed particles, the concentration of the sol and the pH. Spontaneous siloxane bonding in solution is generally not a problem even in concentrated sols if the pH is low (below or close to 2) or if the silica particles are larger than 100 nm in diameter. [3] If siloxane bonds were to form between large silica particles, it is probable that these bonds would break upon collision due to the high mechanical strain within the silica particle. [3]

The rate of siloxane bond formation, or aggregation, increases with temperature. The aggregation is easily distinguished by the formation of gel. Studies show that the sol concentration, the pH and the solvent affect the activation energy of aggregation. Iler has summarized these studies of colloidal silica aggregation in polysilicic acid and the result is showed in Table 1. [3]

Table 1. Colloidal silica aggregation in polysilicic acid. [3]

<i>SiO₂ concentration [%]</i>	<i>pH</i>	<i>Activation energy [kcal mole⁻¹]</i>
20	5.5	10.7
30	5.5	7.6
20	3.0	16.4
30	3.0	11.9

The activation energies were collected from gelling at 23 °C and 60 °C for a deionized sol of 14 nm. [3] It is implied that the pH has a slightly larger effect on the gelling in comparison to the concentration of the sol. This is presumably due to varying particle charge depending on the pH. [3] The silica particles are more electrically neutral when close to pH 2 and negatively charged at higher pH, as previously stated.

The stability of a sol is improved if electrostatic interactions and London forces are present. The strength of the electrostatic interactions between the silica particles are, as previously mentioned, dependent on the pH as it regulates the charge of the silica particles. [3] In case of charged silica particles, the electrostatic interactions separate them as two equally charged particles will repulse one another, stabilizing the system.

London forces are a type of van der Waals interactions, which exist between the particles in a solution. As the electrons fluctuate around the nucleus in an atom, a temporary dipole is created. This temporary dipole can interact with surrounding atoms causing induced dipoles. In a solvent, the short-lived dipole silica molecules can temporarily interact with any existing dipole molecules in the system. [6] The temporary dipoles attract or repel neighboring atoms.

2.2 Drying colloidal silica

It is upon drying of colloidal silica that spontaneous siloxane bonding becomes a problem. As stated, avoiding interactions between the silica particles are crucial to avoid irreversible aggregation, illustrated in Figure 4 below. During drying, the particles are forced together as the media is removed, meaning that siloxane-bond formation only can be prevented by steric stabilization.

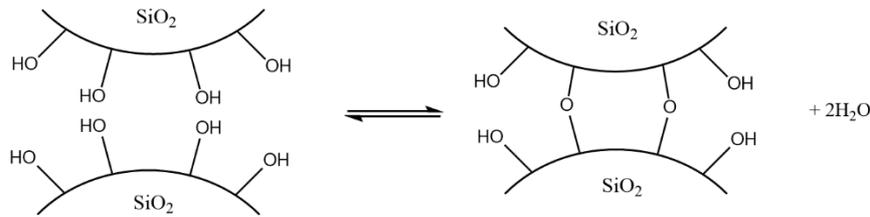


Figure 4. Equilibrium of silanol groups and siloxane bonds at the silica particle surface.

Sterically stabilizing the silica particles with hydrophilic silanes inhibits aggregation both while in solution and during drying. In this specific case, two different hydrophilic silanes were used to hinder the formation of siloxane bonds. Figure 5 below is showing how A) 3-glycidoxypropyl-triethoxy silane (CC) and B) 3-glycidoxypropyl-triethoxy silane and aminopropyl silanes (CCA) were used to stabilize the surface of the colloidal silica.

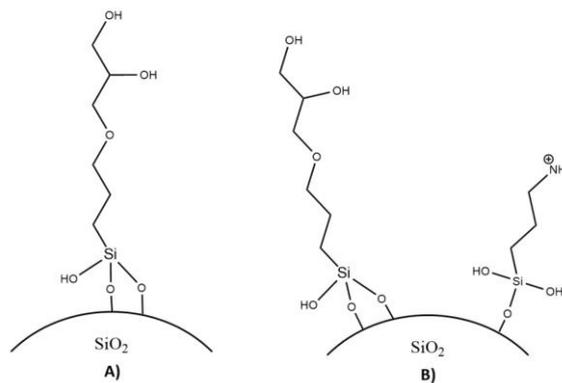


Figure 5. The silica surface of A) CC-silane modified silica and B) CCA-silane modified silica.

As Figure 5 illustrates, the resulting silica particle surface is hydrophilic in both cases.

2.3 Dispersing hydrophilic silica particles

The dispersibility of colloidal silica is varying depending on the solvent. This is due to different dispersion forces present in aqueous and non-aqueous media. The forces present and how they act in the different systems are discussed below.

2.3.1 In aqueous media.

As mentioned earlier, the redispersibility is highly affected by the surface chemistry of the particle and its interaction with the solvent. [7] The redispersibility is also significantly affected by osmotic pressure. The osmotic pressure is caused by an uneven distribution of ions in the system and yields a driving force to eliminate ion concentration gradients throughout the whole system. [7] This is achieved by water flowing into cavities in these ion rich regions and diluting them in these areas. Hence, if the system contains salt, specifically between the dried silica particles, the osmotic pressure can help break up agglomerates of the dried silica, as water penetrates the cavities in these agglomerates. [7]

2.3.2 In non-aqueous media.

The dispersion interactions in organic solvents differ significantly from aqueous systems, as mentioned. Due to low electrostatic interactions in non-aqueous systems, the redispersion of colloidal silica relies on steric repulsion as well as good solvent-surface interactions. Hydrophilic particles have a low wettability in hydrophobic solvents, but it is possible to improve a poor solvent-surface interaction by alteration of the

particle surface. This should be done by matching the surface-modification to a specific solvent to improve the wettability.

2.3.2.1 Redispersion using dispersants

A way to increase the redispersibility of hydrophilic particles in low polarity solvents is by hydrophobizing the surface to promote particle surface-solvent interactions. This could be achieved by the adsorption of dispersants, surface-active species such as surfactants, on the particle surface, as illustrated in Figure 6.

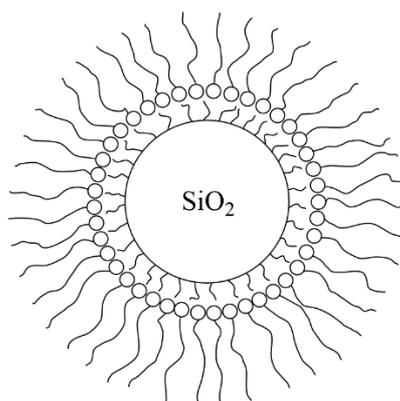


Figure 6. Physisorption of dispersant on the hydrophilic particle surface

The dispersant is illustrated in Figure 6 as a sphere with an attached tail, where the sphere is the polar head group and the attached tail is the hydrophobic alkyl chain. The figure also demonstrates how the hydrophilic head adsorbs to the hydrophilic particle surface, while the hydrophobic part is exposed to the solvent. Contrary to aqueous systems, the hydrophobic effect driving the dispersant to self-assemble at the surface is weak. In organic solvents, dispersant adsorption is a two-part process where the dispersant adsorbs to the surface via electrostatic interaction and/or van der Waal forces, followed by hydrogen bonding or polar interaction between the surfactants and the surface. [8]

2.3.2.2 Redispersion through surface-modification

Another route to increase the redispersibility of hydrophilic particles in non-aqueous systems is by surface modification with hydrophobic groups. The reactant used for such a reaction should have a high propensity to react with the surface, and is dependent on the particle surface and the solvent, as a reaction with surface active groups occurs and the resulting surface ligand should have a good interaction with the surrounding solvent in order to achieve steric stabilization and enhance the wetting by the solvent. [9]

Isocyanates are a group of chemicals that are very reactive. They can have different chemical properties depending on their structure and form covalent bonds as they react with the hydroxyl groups on the CC-silane as shown in Figure 7 below.

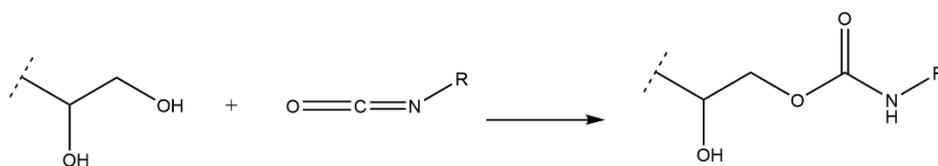


Figure 7. General reaction between CC-silane and isocyanates. One hydroxyl group on the CC-silane and an isocyanate is forming a covalent bond.

As mentioned previously, isocyanates can have different chemical structures and properties. For this study three representative isocyanates were evaluated: A) phenyl isocyanate, B) cyclohexyl isocyanate and C) octadecyl isocyanate. The isocyanate modified particle surface is shown in Figure 8 below.

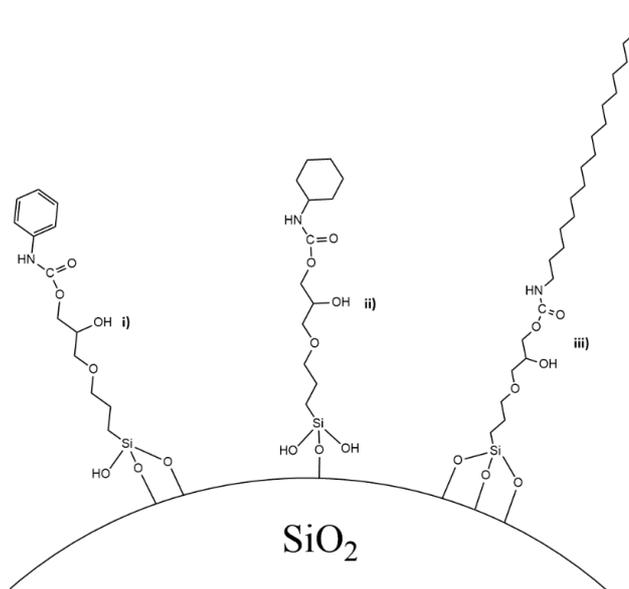


Figure 8. A) Phenyl isocyanate, B) Cyclohexyl isocyanate, C) Octadecyl isocyanate

2.4 Characterization techniques

2.4.1 Scanning electron microscope

Scanning electron microscope (SEM) is an analytical method, operating in vacuum on conductive samples, to provide information about the surface. It can also be coupled with e.g. Energy-Dispersive X-ray spectroscopy, EDX, to give knowledge about the sample surface composition. An electron probe is scanning the sample in straight lines. [10] The instrument creates an image of the sample by analyzing the backscattered and secondary electrons emitted from the sample. The secondary and backscattered electrons provide different information. Secondary electrons come from the sample itself and are released from the outer shells as the sample is bombarded by the electron beam. [10] Hence, they can give precise information about the surface. [11]

The backscattered electrons are primary electrons whose paths are changed due to collision with surface atoms. These electrons give information about the composition as images created from backscattered electrons can illustrate differences in atomic number. The regions consisting of heavier atoms are lighter in comparison to areas of low atomic number atoms, which are darker in the image. Hence, information about the composition can be acquired. [11]

2.4.2 Dynamic light scattering

Dynamic light scattering, DLS, is a common analytical technique for determination of particle size in solution by using light. It is generally used for diluted solutions containing particles of a size less than 1 μm . [12]

Colloidal particles in solution have Brownian motion, meaning they will experience random movement [13]. When the sample is analyzed, particles in solution scatter light in all directions. It is the fluctuation of scattered light with time that is analyzed. Small particles move faster than larger ones, and therefore the changes in scattering intensity will be faster.

Low concentration samples are a prerequisite as higher concentrations result in errors from multiple scatterings [12]. The sample also need to be colloidally stable as in sedimenting particles the motion is dominated by uniaxial flow. [13].

2.4.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a common technique used for investigating the mass loss in relation to time or temperature. The instrument is heating the sample up to a set temperature while reporting the loss of mass. [14] Only a few milligrams of the sample are required to perform the analysis. The thermal degradation of a compound can be measured with TGA analysis. [14]

2.4.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is used to analyze the chemical structure of a compound. The technique is analyzing the sample by irradiating it with infrared light. A detector registers the transmitted radiation and an FTIR spectrum is created. The FTIR spectrum plots demonstrate the absorbance in relation to wavenumber. Each peak is related to a vibration of a bond in the molecule and thus represents specific molecular characteristics. [15] Hence, the chemical structure of a sample can be explored.

3. Materials and methods

3.1 Chemicals

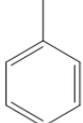
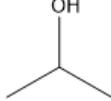
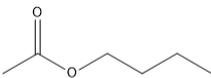
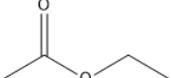
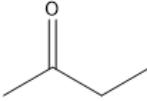
The non-modified silica sol used in this study was provided by Nouryon and had a specific surface area of 130 m²/g. The silanes used to modify the surface are listed in Table 2.

Table 2. Abbreviation and name of the silanes used.

Abbreviation	Name
CC-silane	3-glycidoxypropyl-triethoxy silane
A-silane	3-aminopropyl silane

Throughout the report, samples were prepared in aqueous or non-aqueous media. All solvents used are described in Table 3, where the organic solvents were all of chemical grade. The eight organic solvents are all commonly used solvents with a wide range of polarity.

Table 3. Chemical structure and polarity index for all organic solvents used in the study. [16]¹ [17]²

	<i>Cyclohexane</i> ¹	<i>Toluene</i> ¹	<i>Isopropanol</i> ²	<i>Butyl acetate</i> ¹
				
	Cyclic hydrocarbon	Aromatic hydrocarbon	Alcohol	Ester
<i>Nature of solvent</i>	Non-polar	Non-polar	Polar protic	Polar aprotic
<i>Polarity index</i>	0.2	2.4	4.0	4.0
	<i>Ethyl acetate</i> ²	<i>MEK</i> ²	<i>Ethanol</i> ²	<i>Ethylene glycol</i> ²
				
	Ester	Ketone	Alcohol	Polyhydric alcohol
<i>Nature of solvent</i>	Polar aprotic	Polar aprotic	Polar protic	Polar protic
<i>Polarity index</i>	4.4	4.7	4.3	6.9
	<i>Water</i> ²			
	H ₂ O			
<i>Nature of solvent</i>	Polar protic			
<i>Polarity index</i>	10.2			

Redispersion with dispersants was evaluated in the report. Nine dispersants with different chemical properties were used in combination with the solvents mentioned in Table 3. The chemical structure and charge of all dispersants are illustrated in Table 4.

Table 4. The chemical property and its charge for all dispersants evaluated in the study.

Dispersant	Chemical structure	Ionic/nonionic
A	N-(tallow alkyl)-1,3-propane diamine	Cationic
B	2-propylheptanol + 8 ethylene oxide	Nonionic
C	2-propylheptanol + 5 ethylene oxide	Nonionic
D	2-propylheptanol + 3 ethylene oxide	Nonionic
E	Undercyltriethylene oxide	Nonionic
F	Alkyl phosphate ester	Anionic
G	Alkyl phosphate ester	Anionic
H	Polyamine amide salt	Cationic
I	Alkoxylated alcohol	Nonionic

3.2 Silica nanoparticles surface modification

3.2.1 CC-silane modification

GPTES, CC silane, was hydrolyzed by mixing water at pH ~2.7 and silane, 41:59 water:silane weight ratio. This solution was then added to 5000 g of heated silica sol, while stirring, at a rate of 1 $\mu\text{mol}/\text{m}^2\text{h}$. The temperature was kept at 70 °C until silanes corresponding to a surface coverage of 5 $\mu\text{mol}/\text{m}^2$ had been added and for one subsequent hour. The stirring was maintained overnight after which silane modified sol was poured through a filter. Two batches were produced.

3.1.2 CCA-silane modification

CCA-silane modification consists of 4.5 $\mu\text{mol}/\text{m}^2$ GPTES combined with 0.5 $\mu\text{mol}/\text{m}^2$ aminopropyl silane. The CCA-silane modification procedure is similar to the CC-silane modification with the only exception of the silanes used.

3.1.3 Ion exchange

All batches of modified sol were cation-exchanged while heated to 70 °C. The temperature was maintained for two hours while stirring. The sols were cooled in an ice bath and a subsequent anion-exchange step was performed to pH ~7.

Approximately 2.5 L of the cation-anion exchanged CC- functionalized sol was saved without further treatment, while a cation-exchange step followed for the rest of the sol. Lastly, 2 g/kg sol biocide was added.

Additionally, ~2 L of the CC-functionalized- cation-anion-cation exchanged sol was titrated up to pH 9 using 0.1 M NaOH. ~1 L of the CCA-functionalized cation-anion exchanged sol was divided in two where ammonia was added to one, giving a pH of 9.8, and the other was additionally cation-exchanged, resulting in pH 7.6. This resulted in the five sols mentioned below:

CC functionalized sol

- Cation-anion exchanged at pH 7
- Cation-anion-cation exchanged at pH 2.5
- Cation-anion-cation exchanged, titrated to pH 9

CCA functionalized sol

- Cation-anion-cation exchanged at pH 7.6
- Cation-anion exchanged, titrated to pH 9.8

3.2 Powder production

Six different silica powders of varying properties were used throughout the study. Their abbreviations are created based on the surface modification, ion exchanges and pH. Their abbreviations and properties are demonstrated in Table 5 below.

Table 5. Name and properties for all silica powders used in the study
Silica powder

Abbreviation	Silica powder
CC ⁵ -CAC-2.5	5 μmol CC-silane. Cat-an-cation exchange. pH=2.5
CC ⁵ -CA-7	5 μmol CC-silane. Cat-anion exchange. pH=7
CC ⁵ -CAC-9	5 μmol CC-silane. Cat-an-cation exchange + NaOH. pH=9
CC ⁵ -CA-7-SD	5 μmol CC-silane. Cat-anion exchange. pH=7
CC ^{4.5} A ^{0.5} -CAC-7.6	4.5 μmol CC-silane + 0.5 μmol CCA-silane. Cat-an-cation exchange. pH=7.6
CC ^{4.5} A ^{0.5} -CA-9.8	4.5 μmol CC-silane + 0.5 μmol CCA-silane. Cat-anion exchange + NH ₃ . pH=9.8

3.2.1 Drying

3.2.1.1 Rotary evaporation and oven

CC⁵-CAC-2.5, CC⁵-CA-7, CC⁵-CAC-9, CC^{4.5}-A^{0.5}-CAC-7.6, CC^{4.5}-A^{0.5}-CA-9.8 were all dried by rotary evaporation. Each silica sol was placed in a round bottom flask and dried for a few hours until all visible liquid was removed. The dried silica was then transferred to a beaker and the bigger silica chunks were crushed. The silica was then placed at 110 °C overnight to remove remaining water. Subsequently, the silica was manually ground and stored in plastic containers.

3.2.1.2 Spray drying

CC⁵-CA-7-SD powder was obtained from Nouryon. A CC-modified sol, with a surface coverage of 5 μmol/m², was cation-anion-exchanged and subsequently spray dried.

3.2.2 Ball milling

CC⁵-CAC-2.5, CC⁵-CA-7 and CC⁵-CAC-9 were ball milled to evaluate whether the powder particle size could be reduced to improve redispersion. A sample of each silica was ball milled for 2, 4, 6 and 12 h. The ball milled silica powders were mixed with MilliQ water and put in 90 °C for 24 h. In case of redispersion, particle size was measured. The heating step was then followed by 3 min sonication at 20% amplitude for all samples. The particle size was measured in all samples and compared to non-ball milled samples.

3.3 Redispersion without additives

Three dried silica sols with varying surface modification were evaluated to determine to what extent the drying method and the pH were affecting the redispersion in MilliQ water and ethylene glycol, without the addition of dispersant. All silica powders produced were evaluated: CC⁵-CAC-2.5, CC⁵-CA-7, CC⁵-CAC-9, CC^{4.5}-A^{0.5}-CAC-7.6, CC^{4.5}-A^{0.5}-CA-9.8.

MilliQ water and ethylene glycol were used as solvents due to their similarity in polarity. Figure 9 shows the route for particle size evaluation in the solvents without any additives.

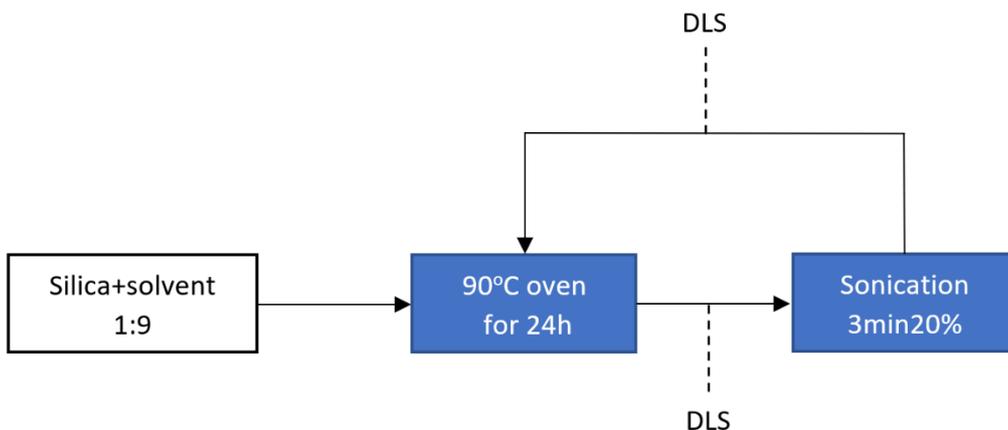


Figure 9. Schematic illustration of the route of silica redispersion in MilliQ water and ethylene glycol, without additives.

As Figure 9 illustrates, 1 ± 0.03 g of silica was mixed with 9 ± 0.03 g of solvent and put at 90°C for 24 h, followed by 3 min sonication at 20% amplitude for all samples. Particle size was determined by DLS, if the sample was redispersed. A redispersed sample is characterized as a sample where the silica agglomerates show no appreciable sedimentation. Heating and sonication treatments were repeated until the samples had regained their initial particle size or, in one case, until the solvent had evaporated and treatments were no longer possible.

3.4 Redispersion using additives

Nine dispersants were evaluated on their ability to improve the redispersibility of silica in nine solvents. To limit the number of analyses, a 1:1 dispersant to silica ratio was employed and if the sample showed enhancement compared to the silica-solvent mixture alone, 2:1 and 3:1 dispersant to silica ratios were also examined. Samples containing a dispersant to silica ratio less than 1:1 was previously examined but as no improvement was visible, higher dispersant:silica ratios were selected. Calculations regarding the amount of dispersant added are found in Appendix I. The general experimental plan is described in Figure 10.

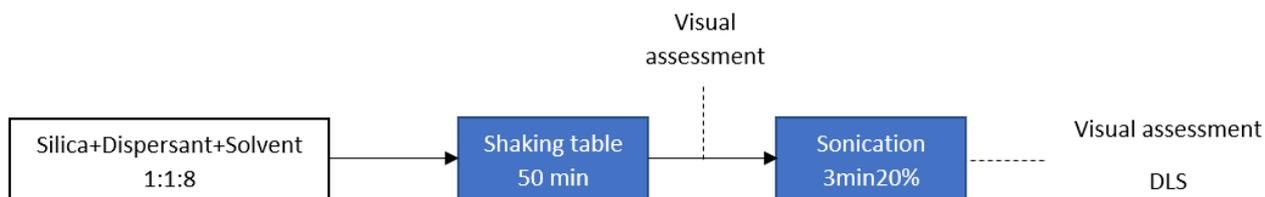


Figure 10. Experimental plan for dispersant route

Firstly, the dispersant was mixed with the solvent on a shaking table for 10 min. If the dispersant neither dispersed nor dissolved, the sample vial was put in hot water and back on the shaking table, and if there was no change the sample was removed. This was followed by addition of silica which had been additionally dried at 180°C for 1 h in order to remove the remaining water. The samples were then shaken for 50 min at 210 rpm, followed by 3 min sonication at 20%. The samples contained a total of 1 ± 0.03 g silica, 1 ± 0.03 g dispersant and 8 ± 0.03 g solvent. A DLS analysis was performed if the silica redispersed.

This investigation mainly focused on the CC⁵-CAC-2.5 powder. However, additional testing was performed using the CC⁵-CA-7-SD, CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 powders. The samples made can be seen in Table 6 below.

Table 6. Samples made, checked boxes indicates which solvent-dispersant combinations that were tested.

CC⁵-CAC-2.5	<i>Ref</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>
<i>T</i>	√	√	√	√	√	√	√	√	√	√
<i>CH</i>	√	√	√	√	√	√	√	√	√	√
<i>BA</i>	√	√	√	√	√	√	√	√	√	√
<i>EA</i>	√	√	√	√	√	√	√	√	√	√
<i>MEK</i>	√	√	√	√	√	√	√	√	√	√
<i>IP</i>	√	√	√	√	√	√	√	√	√	√
<i>E</i>	√	√	√	√	√	√	√	√	√	√
<i>EG</i>	√	-	√	√	√	√	-	√	-	√
CC⁵-CA-7-SD										
<i>T</i>	√	-	-	-	√	-	-	-	-	√
CC^{4.5}-A^{0.5}-CAC-7.6										
<i>T</i>	√	-	-	-	√	-	√	-	-	√
<i>CH</i>	√	-	-	-	√	-	√	-	-	√
<i>EA</i>	√	-	-	-	√	-	√	-	-	√
<i>IP</i>	√	-	-	-	√	-	√	-	-	√
CC^{4.5}-A^{0.5}-CA-9.8										
<i>T</i>	√	-	-	-	√	-	√	-	-	√
<i>CH</i>	√	-	-	-	√	-	√	-	-	√
<i>EA</i>	√	-	-	-	√	-	√	-	-	√
<i>IP</i>	√	-	-	-	√	-	√	-	-	√

All samples regarding redispersion with additives are evaluated based on the amount of sediment phase as well as the amount of light sediment on top. The light sediment is not compact as the bottom sediment phase. The light sediment is also relatively mobile, e.g. the lighter sediment moves with the motion when the sample vial is tilted. Figure 11 is demonstrating the definition of the two different types of sediment.

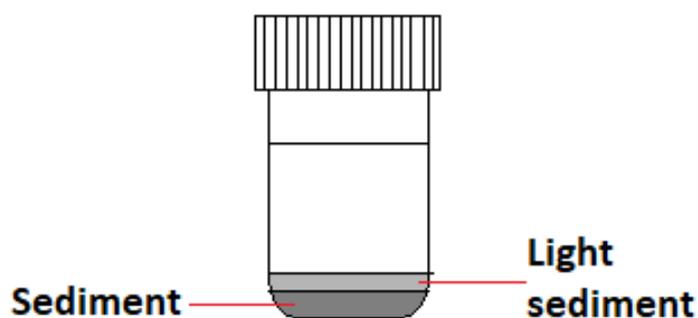


Figure 11. Image illustration the definition of the sediment phase and the light sediment phase in samples were silica was redispersed with additives.

Using heat for dispersion

Some samples prepared in toluene were heated to 70 °C for 24h, following the sonication route described in Figure 9, to examine whether heating would improve the redispersibility of silica. The samples where heat was used as a parameter are displayed in Table 7 below.

Table 7 All samples tested at elevated temperature.

<i>CC</i> ⁵ - <i>CAC</i> -2.5	<i>Ref</i>	<i>D</i>	<i>F</i>	<i>I</i>
<i>T</i>	√	√	-	√
<i>CC</i> ⁵ - <i>CA</i> -7- <i>SD</i>				
<i>T</i>	√	√	-	√
<i>CC</i> ^{4.5} - <i>A</i> ^{0.5} - <i>CAC</i> -7.6				
<i>T</i>	√	√	√	√
<i>CC</i> ^{4.5} - <i>A</i> ^{0.5} - <i>CA</i> -9.8				
<i>T</i>	√	√	√	√

3.4.1 Adding dispersant prior to drying

Dispersant was added to the silica sol before drying to evaluate its effect on the redispersibility of silica in organic solvent. According to calculations, roughly 0.1 g of dispersant per g powder is required to achieve a dispersant monolayer on the colloidal silica. Dispersant *B*, *E* and *I* were chosen as they seemed to perform the best in toluene. Dispersant was added to the silica sol and placed at 110 °C overnight. The dried powder was ground, and 1.1 g was redispersed in toluene.

The wetting agent PEG was examined as well, as it present solubility in both water and toluene. 15% PEG in relation to the amount of silica was added to the silica sol and dried as previously stated. The resulting powder was ground, and 1.15 g was redispersed in toluene.

3.5 Surface modification with isocyanates

3.5.1 Effect of bound water

Phenyl isocyanate, cyclohexyl isocyanate and octadecyl isocyanate were used to modify the surface of the colloidal silica to promote redispersion. Whether removal of the tightly bound water was affecting the redispersion was examined by comparing samples of silica additionally dried in 180 °C and non-additionally dried silica, in toluene and with each isocyanate. All samples were performed by stirring for up to 24 h. Table 8 provides the isocyanate ratios used in all samples. The ratios are based on the amount of isocyanate needed to form a monolayer on the silica particles, if an isocyanate reacted with one of the two hydroxyl groups on the CC-silane. All calculations are found in Appendix I.

Table 8. Isocyanate ratios for evaluation of the effect of bound water.

Isocyanate	Ratio [Isocyanate:silica]
Phenyl	1:1
Cyclohexyl	2:1
Octadecyl	2:1

Figure 12 below is demonstrating how the evaluation of additionally dried silica versus non-additionally dried silica was performed.

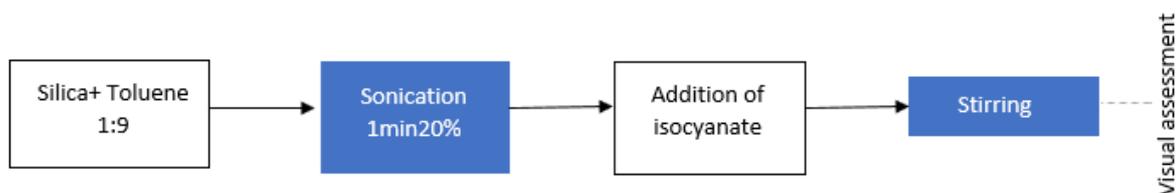


Figure 12. Evaluation of additionally dried versus non-additionally dried silica.

3.5.2 Effect of reaction conditions

One hydroxyl group on each diol was deemed to be able to react, and the ratio of isocyanate in relation to active sites on the silica was calculated. A 1:1 isocyanate:silica ratio means that the amount of isocyanates added corresponds to the reaction of one hydroxyl group on each diol present on the silica surface.

The effect of reaction conditions was evaluated by preparing and comparing samples in toluene. Three different methods were evaluated based on the height of the turbid phase of each sample. 1 ± 0.03 g of CC⁵-CAC-2.5 was mixed with 9 ± 0.03 g toluene and sonicated for 1 minute at 20% amplitude, regardless of the method. Surface modification was then carried out by the three different methods:

- Stirring: Using a magnetic stirrer
- Sonication: Ultrasonic bath 2x 90 min followed by stirring
- Hot bath: Magnetic stirring in a 40 °C water bath

Isocyanates were added according to the ratios stated in Table 9 and all samples were let to react for up to 48 h.

Table 9. Isocyanate ratios used for evaluation of reaction method

Isocyanate	Ratio [Isocyanate:silica]
Phenyl	3:2
Cyclohexyl	3:1
Octadecyl	3:1

Figure 13. is illustrating the how the method evaluation was performed.

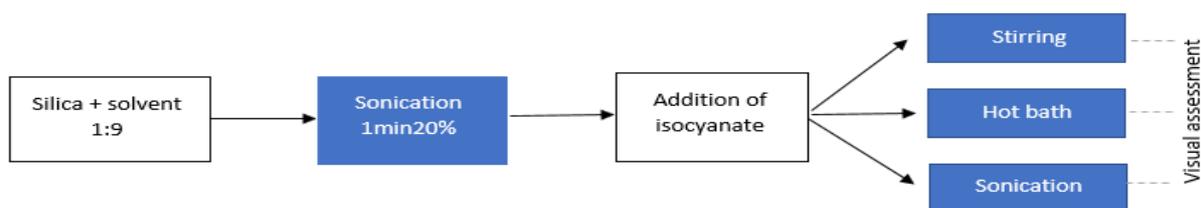


Figure 13. Reaction scheme of evaluation of reaction method.

All samples regarding the isocyanate surface modification route were evaluated based on the amount of sediment at the bottom as well as the height of the turbid phase. Figure 14 is illustrating the definition of a sediment and of a turbid phase.

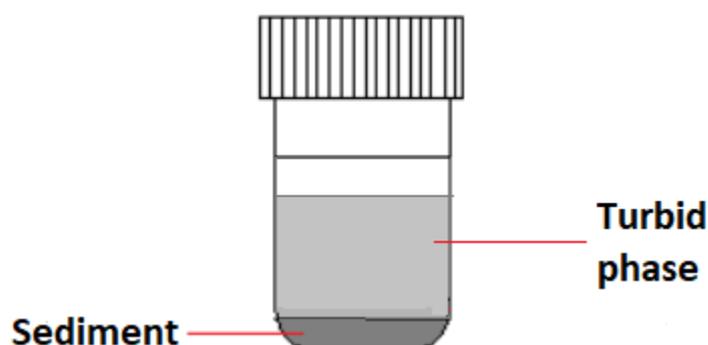


Figure 14. Description of an isocyanate surface modified sample containing a sediment phase, a turbid phase and a clear phase.

3.5.3 Effect of solvent

Surface modification of CC⁵-CAC-2.5 was also performed in cyclohexane, ethyl acetate and MEK using the stirring method, as well as CC⁵-CA-7-SD in toluene for reference.

3.6 Characterization techniques

3.6.1 SEM

All silica powders were analyzed in SEM. The samples were prepared by pressing each powder onto a SEM sample holder and coated with palladium.

3.6.2 TGA

The remaining water in CC⁵-CAC-2.5, CC⁵-CA-7-SD, CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 was determined by TGA. Approximately 8 mg of CC⁵-CAC-2.5 and CC⁵-CA-7-SD powders were used and approximately 5 mg of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8. Analysis were performed by heating the samples starting from a temperature of 30 °C up to 600 °C, with a rate of 10 °C/min. The mass loss was measured in relation to increased heat.

The removal of water is assumed to be completed at the onset of the sharp mass loss in the curve, as shown in the appendix. This mass loss is presumably due to the degradation of the silane surface modification.

3.6.3 DLS

0.1 ml of sample was diluted in 9.9 ml solvent, the solvent depending on the sample. Samples of aqueous media were diluted in 0.02 M NaCl and non-aqueous samples were diluted in their solvent. Approximately 1 ml of diluted sample was transferred to a vial. Plastic cuvettes were used for aqueous samples and crystal glass cuvettes were used for non-aqueous samples. These vials were then used for DLS analysis.

3.6.4 FTIR

FTIR was performed to evaluate whether the isocyanates had successfully reacted with the silanes. It was performed on three samples containing CC⁵-CA-7-SD, toluene and one of the three isocyanates. The toluene was removed from the samples by evaporation in a fume hood and the dried silica-isocyanate powder was used for the FTIR analysis. Approximately 3 mg of the dried sample was mixed with 300 mg KBr and pressed into tablets. The prepared tablets were then analyzed.

4. Results and discussion

4.1 Sol production

While performing the ion exchanges on the CC-modified sol, a significant increase in viscosity was observed in the anion exchange step, where the pH was increased from pH ~2 to pH~7. A DLS showed that the particle size was unaffected, and after the subsequent cation exchange, where the pH once again was decreased to pH~2 the initial viscosity was regained. Hence, the increase in viscosity is likely due to an electroviscous effect.

While producing the CCA-modified sol, a color change could be observed when increasing the pH with ammonia. A DLS showed that the particle size had increased from 33 nm to 46.6 nm, i.e. the particles had aggregated.

4.2 Powder production

The drying process resulted in silica powders with different amounts of tightly bound water. TGA was done on CC⁵-CAC-2.5, CC⁵-CA-7-SD and both the CCA-modified powders to determine the water content, as found in Appendix II. The analyses stated that the CC-modified powders had roughly 1 wt.% water, while the CCA-modified powders both had approximately 0.5 wt.% tightly bound water.

4.2.1 Effect of drying method

Figure 15 shows SEM images of rotary evaporated CC⁵-CAC-2.5, CC⁵-CA-7 and CC⁵-CAC-9 powders in 500x magnification while Figure 16 is showing CC⁵-CA-7-SD, CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 in 2000x magnification.

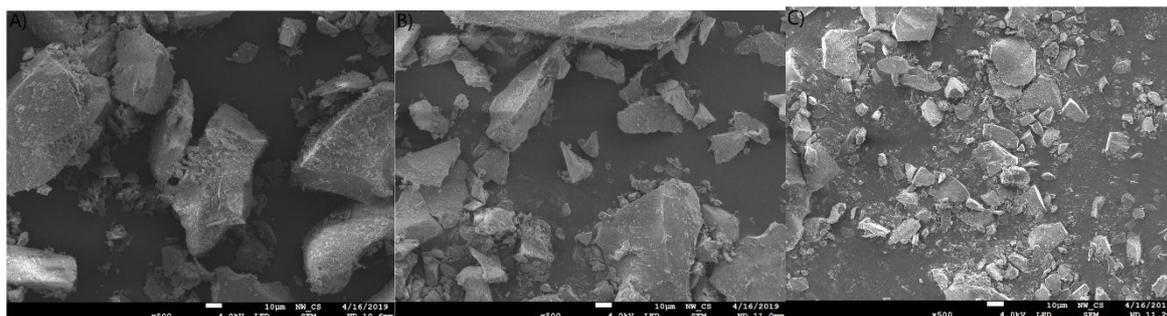


Figure 15 from left to right: A) SEM image of CC⁵-CAC-2.5 in 500x magnification. B) SEM image of CC⁵-CA-7 in 500x magnification. C) SEM image of CC⁵-CAC-9 in 500x magnification.

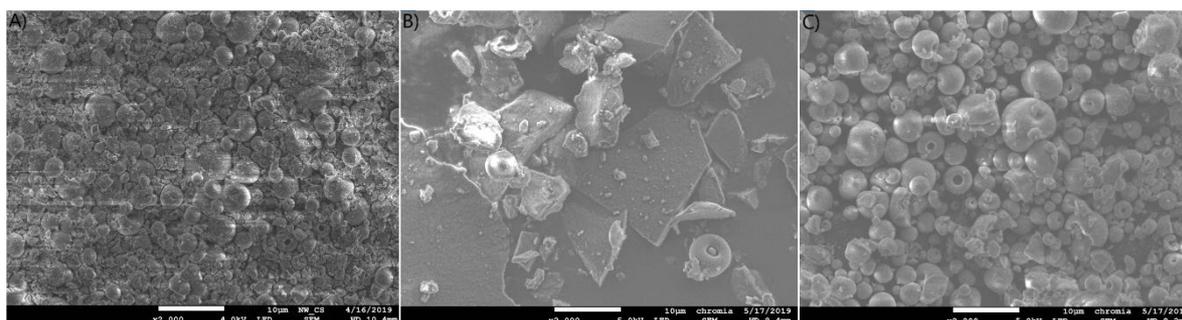


Figure 16. From left to right: A) SEM image of CC⁵-CA-7-SD in 2000x magnification B) SEM image of CC^{4.5}-A^{0.5}-CAC-7.6 in 2000x magnification. C) SEM image of CC^{4.5}-A^{0.5}-CA-9.8 in 2000x magnification.

As seen above, the CC⁵-CAC-2.5, CC⁵-CA-7 and CC⁵-CAC-9 look similar with rough, rugged particles containing larger agglomerates. The spray dried silica has round raspberry like particles with a small agglomerate size. The CC^{4.5}-A^{0.5}-CAC-7.6 is similar to the rotary evaporated CC-modified powders, with its rugged agglomerates. It does, however, also contain few round particles as seen in the right corner of figure 16 B). The CC^{4.5}-A^{0.5}-CA-9.8 powder is entirely made up of small round particles. In that sense, the CC^{4.5}-A^{0.5}-CA-9.8 powder is

similar to the spray dried CC^5 -CA-7-SD. However, as the image suggests, the CC^5 -CA-7-SD powder seems to consist of aggregates smaller in size, compared to the other powders.

The differences in shape of the powder particles between the CC^5 -CAC-2.5, CC^5 -CA-7, CC^5 -CAC-9 and CC^5 -CA-7-SD can be attributed to the different drying methods. However, $CC^{4.5}$ -A^{0.5}-CAC-7.6 and $CC^{4.5}$ -A^{0.5}-CA-9.8 differed significantly despite of the same drying method being used. The ammonia in the $CC^{4.5}$ -A^{0.5}-CA-9.8 sol may be the reason to why the dried silica powder gets its round shape. As water evaporates, the ammonia solubility limit is reached and ammonia gas is subsequently removed, which might inhibit the formation of physical bonds, leading to faceted aggregates, between the particles resulting in a round agglomerate shape.

4.2.2 Ball milling

To evaluate whether decreasing the particle size of the powder by physically grinding it in a ball mill influenced redispersion, samples were prepared from CC^5 -CAC-2.5, CC^5 -CA-7 and CC^5 -CAC-9 and taken in a range from 0 h ball milling to 12 h ball milling. The redispersion method followed the method for samples prepared without additives. CC^5 -CA-7 and CC^5 -CAC-9 redispersed after only 90 °C heating treatment for 24 h. Hence, the particle size was measured both before and after sonication. Figure 17 is showing the measured particle size of the redispersed sample in relation to ball milling time. The particle size data is found in Appendix III.

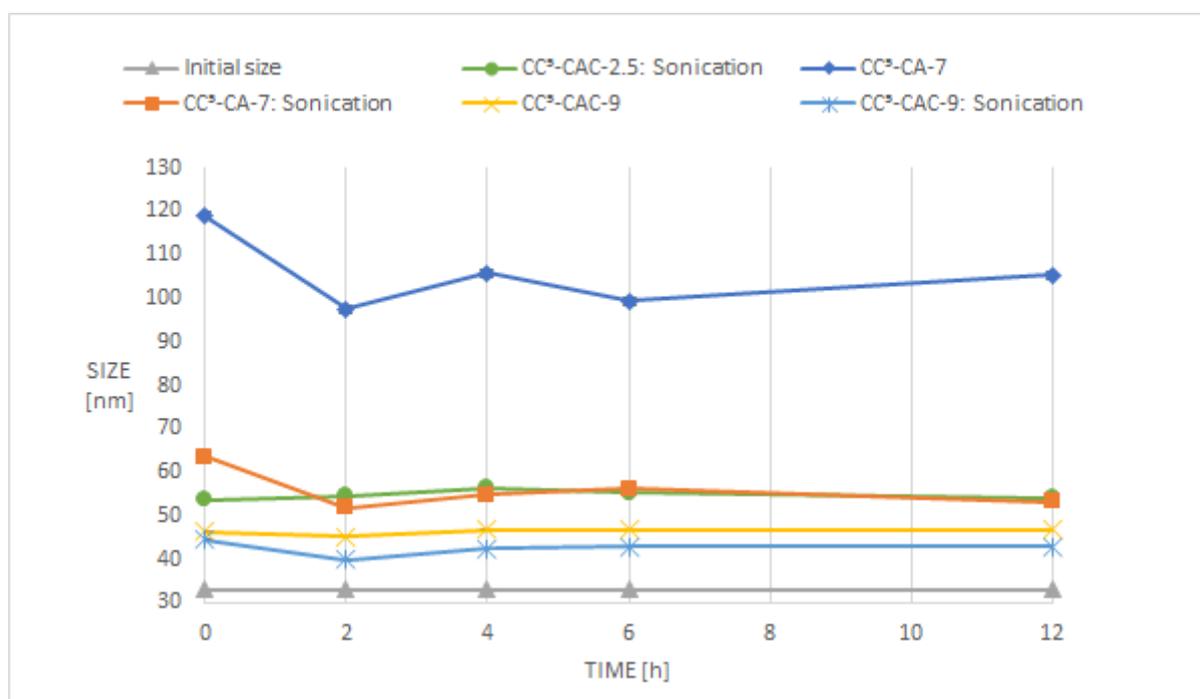


Figure 17. The particle size of the redispersed samples containing CC^5 -CAC-2.5, CC^5 -CA-7 or CC^5 -CAC-9, which has been ball milled for 0, 2, 4, 6 or 12 h. The initial particle size of the sol is added for comparison.

As seen above, ball milling made no significant difference for any samples except the CC^5 -CA-7 powder. The CC^5 -CA-7 powder size decreased from 119 nm to 97.5 nm in particle size after 2 h ball milling, when evaluating the size of the redispersed samples after 24 h at 90 °C. The reason for this may however be due to poor manual grinding before the ball milling step. The CC^5 -CAC-2.5 and CC^5 -CAC-9 had smaller powder agglomerated already after drying and were also grinded manually for a longer time prior to ball milling. Once a certain agglomerate size was reached, the redispersion was not improved by ball milling. This is clear as the particle size of the CC^5 -CAC-2.5- and CC^5 -CAC-9 samples had no correlation to the ball milling time.

Additionally, sonication makes an extensive impact on particle size when larger agglomerates are present., as when dispersing the poorly ground CC⁵-CA-7 powder, a 3 min sonication at 20% amplitude decreased the particle size by approximately 50 nm, regardless of the ball milling time.

4.3 Redispersion without additives

4.3.1 Redispersion in water

It was possible to redisperse all silica powders in MilliQ water, with varying amounts of treatment steps. The ambition was to redisperse the powder and reach the initial particle size, measured in the silica sol. Each silica sol had slightly different particle size and are displayed in the table below.

Table 10. Table illustrating the measured particle size of all silica sols

Sample	Particle size [nm]
CC ⁵ -CAC-2.5, CC ⁵ -CA-7, CC ⁵ -CAC-9, CC ⁵ -CA-7-SD	33.0
CC ^{4.5} -A ^{0.5} -CAC-7.6	46.6
CC ^{4.5} -A ^{0.5} -CA-9.8	32.1

Figure 18 illustrates how the particle size of the CC-powders varied depending on the number of treatment steps. The particle size data is found in Appendix IV.

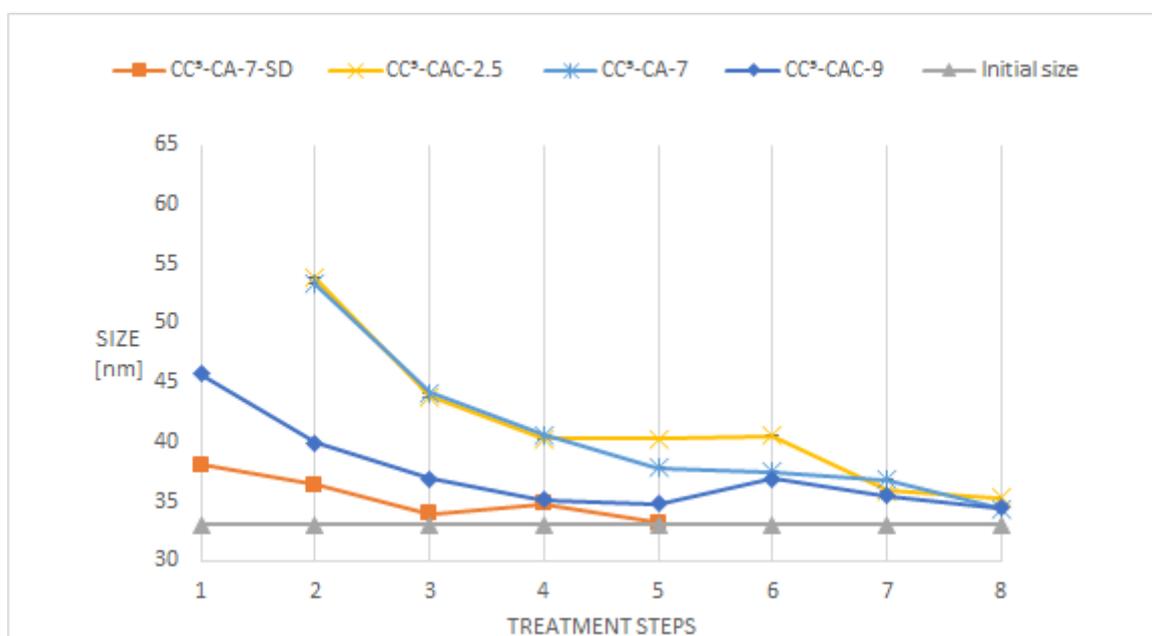


Figure 18. The measured particle sizes of CC⁵-CAC-2.5, CC⁵-CA-7, CC⁵-CAC-9 and CC⁵-CA-7-SD silica redispersed in MilliQ water.

The samples in Figure 18 were exposed to a variation of treatments, all described in Table 11.

Table 11. Treatment steps water-silica samples

Treatment step	1	2	3	4	5	6	7	8
Hours 90 °C	24h	24h	24hx2	24hx2	24hx3	24hx4	24hx6	24hx10
Sonication	-	x1	x1	x2	x2	x3	x3	x3

As seen in Figure 18, CC⁵-CA-7-SD and CC⁵-CAC-9 had been redispersed after only 24 h at 90 °C, while CC⁵-CAC-2.5 and CC⁵-CA-7 both needed sonication in order to redisperse without a sediment. This is notable as CC⁵-CA-7, during ball milling evaluation, redispersed by simply elevating the temperature. These differences are likely due to slightly different times in the oven, where the decreased time at 90 °C was detrimental for

redispersion of CC⁵-CA-7. It might also be due to different agglomerate sizes of the powders as the agglomerate size distribution was broad.

The difference in energy input required for the different silica powders to reach the initial particle size is due to the varying coarseness of the powders. CC⁵-CA-7-SD is a much lighter and finer powder compared to the rotary evaporated CC-modified powders. Hence, fewer treatment steps were required to reach the initial particle size. The roughness of the powder is directly correlated to the drying method, where the spray dried CC⁵-CA-7-SD powder has smaller agglomerates, i.e. has a larger total surface area. Subsequently, the interaction with the solvent is better compared to the rougher powders as more surface is exposed to and can be wetted by the solvent. Hence, rough powders need more energy input to regain their initial particle size as the interaction with the solvent is lower.

CC⁵-CA-7-SD and the CC⁵-CA-7 silica have similar pH, yet CC⁵-CA-7 needs more energy input to redisperse, further supporting the explanation that the drying method and the size of the agglomerates affects the redispersion more in comparison to pH.

As seen in Figure 18, CC⁵-CAC-9 redisperses after the first treatment step, just like CC⁵-CA-7-SD. This might be due to the presence of salt. Since the CC⁵-CAC-9 silica sol was prepared by adding NaOH to the CC-modified cat-an-cation exchanged silica sol, sodium ions are present between the dried silica particles. Due to the osmotic effect in water, the sodium is helping the agglomerated silica particles to separate, promoting solvent interaction by increasing the total surface exposed to the solvent. This would explain why the CC⁵-CAC-9 silica is redispersing while the CC⁵-CAC-2.5 is not.

This could also explain why CC⁵-CA-7 can be redispersed by elevating the temperature alone; ions on the surface of the primary particles cause an osmotic gradient, yielding pressure. However, this osmotic pressure is significantly lesser than that of CC⁵-CAC-9 as no additional salt has been added. Hence, redispersion of CC⁵-CA-7 was affected by agglomerate size of the powder and time in the oven to a greater extent compared to CC⁵-CAC-9.

Salt was added to tap water and samples containing CC⁵-CAC-2.5 and CC⁵-CAC-9, and the ion rich water solutions were prepared to examine whether the redispersion was affected. These samples can be seen after they had been redispersed in Figure 19, along with their references containing 10 wt.% silica prepared from their silica sols.



Figure 19. Evaluation of osmotic force. From left to right: CC⁵-CAC-2.5 reference, CC⁵-CAC-2.5 with addition of salt, CC⁵-CAC-9 reference and CC⁵-CAC-9 with addition of salt.

After 24 h in 90 °C, the CC⁵-CAC-9 sample had not been redispersed. Comparing with the CC⁵-CAC-9 samples prepared in MilliQ water, an additional sonication step was needed for the sample to be redispersed showing that the redispersibility was affected by the additional ions present. A DLS analysis revealed that the CC⁵-CAC-2.5 powder had a smaller particle size, 42.7 nm compared to the 50.8 nm particle size of the CC⁵-CAC-9 sample. The Table below shows the difference between the ion-rich samples and the samples made in milliQ water after 24 h in 90 °C and 3 min sonication at 20% amplitude.

Table 12. Difference in particle size

Sample	Ion-rich water	MilliQ water
Particle size of CC ⁵ -CAC-2.5 [nm]	42.7	53.8
Particle size of CC ⁵ -CAC-9 [nm]	50.8	39.9

As displayed in Table 12, the particle size of CC⁵-CAC-2.5 is decreased when in ion-rich media. However, this might be due to variations in the powder agglomerate size added to the ion-rich sample in comparison to the MilliQ water sample. This experiment also showed that CC⁵-CAC-9 redisperses after fewer treatment steps in MilliQ water, compared to ion-rich water. This might be due to an osmotic pressure, which is decreased when ions are present in solution. It might also be due to salt screening of the particles, decreasing the particle repulsion and consequently a strong driving force for redispersion, but is likely a combination of the two.

The redispersion of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 in MilliQ was also evaluated. Figure 20 is demonstrating how the particle size of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 in MilliQ water depends on the number of treatment steps. The particle size data for the CCA-modified silica is found in Appendix IV.

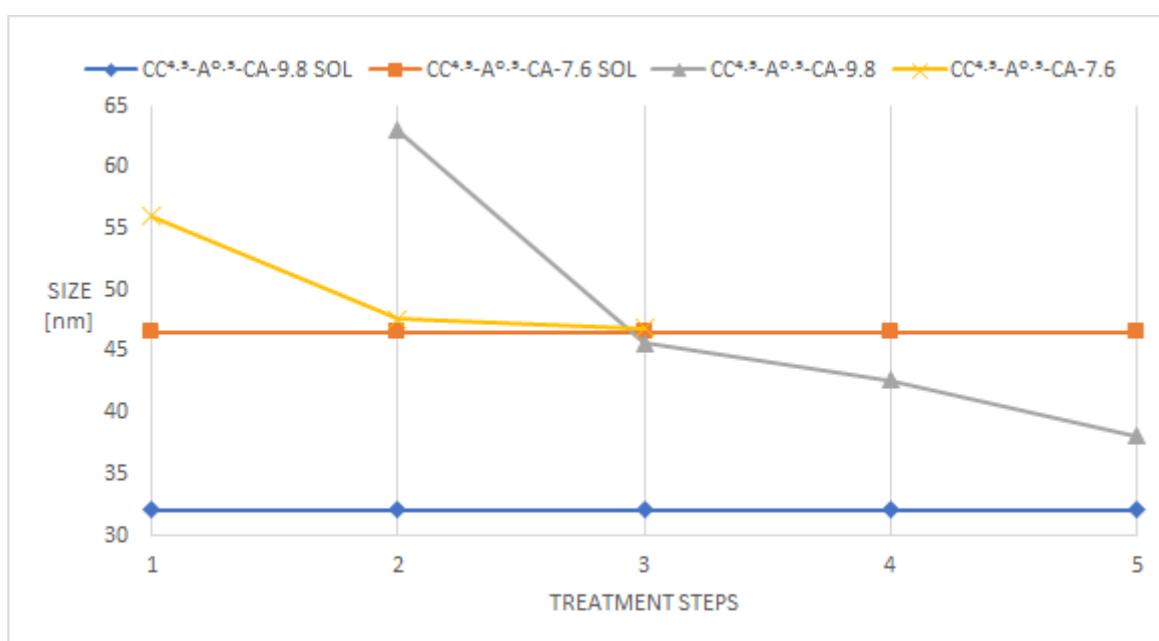


Figure 20. The measured particle sizes of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 redispersed in MilliQ water.

The samples in Figure 20 were exposed to a variation of treatments, all described in Table 13.

Table 13. Treatment steps water-silica samples

Treatment step	1	2	3	4	5
Hours 90 °C	24h	24h	24hx2	24hx2	24hx3
Sonication	-	x1	x1	x2	x2

As seen in Figure 20, the CC^{4.5}-A^{0.5}-CAC-7.6 reached its initial particle size after only three treatments steps while CC^{4.5}-A^{0.5}-CA-9.8 showed its smallest size after five treatments steps. As mentioned earlier, it was not possible to reach the initial size when redispersing the CC^{4.5}-A^{0.5}-CA-9.8 as the sample evaporated with continued treatments. The sample evaporation is likely due to the sample not being completely sealed in the oven. There is no osmotic effect with CC^{4.5}-A^{0.5}-CA-9.8, as the ammonia was removed during drying. Hence, there is no salt present when the silica is redispersed in MilliQ water.

Furthermore, the difference in energy input needed to redisperse $CC^{4.5}-A^{0.5}-CAC-7.6$ and $CC^{4.5}-A^{0.5}-CA-9.8$ might be due to the bigger initial particle size of $CC^{4.5}-A^{0.5}-CAC-7.6$, as the particles aggregated during production yielding a product with a larger starting particle size. Additionally, the smaller agglomerates of the $CC^{4.5}-A^{0.5}-CAC-9.8$ did not help redispersion suggesting that surface modification has a great effect on redispersion as well.

As stated earlier, both the drying method and presence of ions affect the redispersibility, but to a different extent. Addition of sodium hydroxide before drying the sol is promoting the breakage of bigger agglomerates at an early stage due to the osmotic force, but it does not seem to accelerate the redispersion in the sense that less energy is required to regain the initial particle size. This is demonstrated by the fact that all rotary evaporated silica powders reach its initial size after the same number of treatments, no matter the pH.

Surface modification also greatly affects the energy input required for redispersion. This is suggested by the fact that $CC^5-CA-7-SD$ and $CC^{4.5}-A^{0.5}-CAC-7.6$ reach their minimum particle size after only five treatments, despite the variation in roughness of the powders. This indicated that $CC^{4.5}-A^{0.5}-CAC-7.6$ has a better surface-solvent interaction than $CC^5-CA-7-SD$, i.e. that the diol-amine modification has a better interaction with water than the diol modification alone.

All evaluated samples after their final treatment are visible in Figure 21 A)-C). Figure 21 A) and B) illustrates the $CC^{4.5}-A^{0.5}-CA-9.8$ and $CC^{4.5}-A^{0.5}-CAC-7.6$ in comparison to their reference containing a 10 wt.% silica sample prepared from the silica sol. $CC^5-CA-7-SD$, $CC^5-CAC-2.5$, CC^5-CA-7 and $CC^5-CAC-9$ is displayed in 21 C).

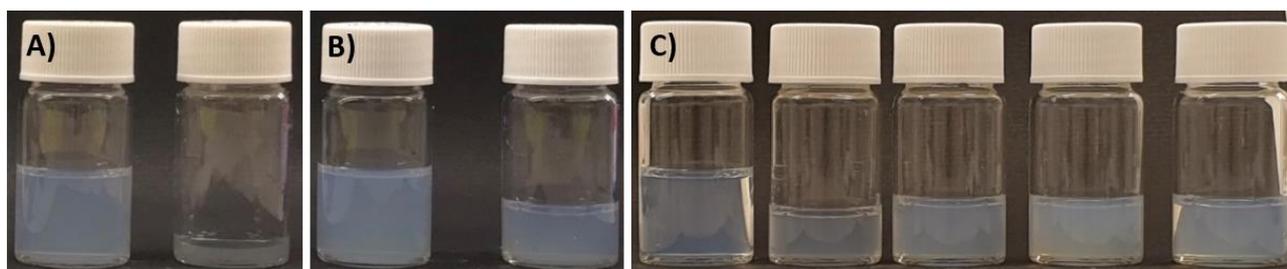


Figure 21. From left to right: A) $CC^{4.5}-A^{0.5}-CA-9.8$ reference $CC^{4.5}-A^{0.5}-CA-9.8$ sample after final treatment B) $CC^{4.5}-A^{0.5}-CAC-7.6$ reference and $CC^{4.5}-A^{0.5}-CAC-7.6$ after final treatment C) Ref, $CC^5-CAC-2.5$, CC^5-CA-7 , $CC^5-CAC-9$ and $CC^5-CA-7-SD$.

4.3.2 Redispersion in ethylene glycol

Attempts were made to redisperse the different silicas in ethylene glycol. However, it was only possible to redisperse $CC^5-CA-7-SD$ but impossible to reach the initial size of 33 nm. The remaining silicas had a sediment even after 30 days in 90 °C and multiple sonication steps, and despite the very high viscosity of ethylene glycol.

The particle size of spray dried silica in ethylene glycol was approximately 90 nm for most of the measurements. Continued treatments did not result in any decreased particle size as well as no significant change in polydispersity index. The measured particle size in relation to treatment steps are illustrated in Figure 22. All DLS data is found in Appendix V.

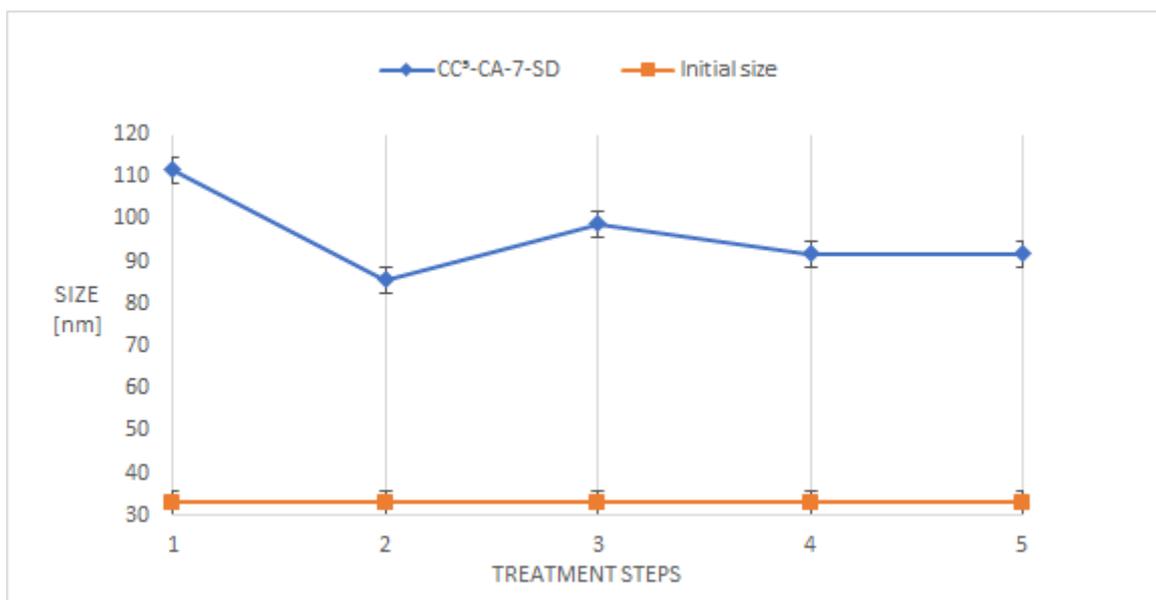


Figure 22. Redispersion of spray dried silica in ethylene glycol.

The CC⁵-CA-7-SD in Figure 22 was exposed to the treatments described in Table 14.

Table 14. Treatment steps

Treatment step	1	2	3	4	5
Hours 90 °C	24hx3	24hx4	24hx5	24hx8	24hx9
Sonication	x3	x4	x5	x6	x6

All CC-modified- and CCA- modified powder samples in ethylene glycol were exposed to the same treatments, stated in Table 13 above. However, only CC⁵-CA-7-SD showed an improvement and continued treatments after treatment step 5 showed no change in size or polydispersity index. Hence, no further treatments were applied. All samples after final treatment are illustrated in Figure 23, where the samples that had not been redispersed were exposed to 30 days 90 °C and multiple sonication steps, still resulting in sedimented samples.



Figure 23 . CC⁵-CAC-2.5, CC⁵-CA-7, CC⁵-CAC-9, CC⁵-CA-7-SD, CC^{4.5}-A^{0.5}-CA-9.8 and CC^{4.5}-A^{0.5}-CAC-7.6 after final treatment in ethylene glycol.

Compared to aqueous systems, the driving forces present for redispersion in ethylene glycol are weaker. In water, the diols on the CC-modification are well hydrated and there is an electrosteric repulsion along with osmotic pressure, all of which are weaker in ethylene glycol. Hence, the redispersion is low due to the lack of a driving forces for redispersion in the organic solvents. The agglomerate size of the dried silica is therefore affecting the redispersibility to a higher extent in organic solvent than in aqueous media. The inclusion of salt is not making a difference either as the osmotic forces in ethylene glycol are weak. A different redispersion method or an altered surface modification is necessary to achieve a better redispersion in ethylene glycol to regain the initial size.

4.4 Redispersion using additives

4.4.1 Redispersion of silica with diol-covered surface

The redispersibility of dried diol-modified silica, CC⁵-CAC-2.5, was investigated in all eight organic solvents using the various dispersant. Reference samples containing only silica were produced for comparison in each solvent. Table 15 describes the reference and if and how each sample deviated from the reference.

Table 15. How each dispersant sample deviates from their reference.

	<i>Ref</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>
<i>T</i>	<i>LS, CS</i>	<i>N/D</i>	<i>>LS</i>	<i>>LS</i>	<i>>LS</i>	<i>ND</i>	<i>>LS,>SH</i>	<i>ND</i>	<i>ND</i>	<i>>LS,>SH</i>
<i>CH</i>	<i>LS, CS</i>	<i>ND</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>	<i><LS</i>	<i>>LS</i>	<i>ND</i>	<i>ND</i>	<i>>LS</i>
<i>BA</i>	<i>LS, CS</i>	<i>WP</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>
<i>EA</i>	<i>LS, CS</i>	<i>WP</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>
<i>MEK</i>	<i>LS, CS, SS</i>	<i>WP</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
<i>IP</i>	<i>LS, CS, SS</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
<i>E</i>	<i>LS, CS, SS</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
<i>EG</i>	<i>SS, CS</i>	-	<i>ND</i>	<i>ND, SS</i>	<i>ND</i>	<i>ND</i>	-	<i>>V</i>	-	<i>ND</i>

ND-No deviation

LS-Light sediment

CP-Compact sediment

V-Viscous

SS-Slow sedimentation

SH- Sediment height

As Table 15 states, most samples has the same sediment height as the reference and no significant deviation from the reference can be observed, all samples are pictured in Appendix VI. Most samples, even the references, displayed the three-phase system previously mentioned in the experimental part with a lighter sediment at the solvent-sediment interface and a heavier, compact sediment at the bottom.

The varying type of sediment strongly indicates that the interaction between the solvent, dispersant and the silica surface differ. The light sediment is temporarily redispersible upon shaking and has a significantly decreased rate of sedimentation compared to the compact sediment. Subsequently, samples containing these light sediments were deemed more successful, however, no sample fully redispersed, meaning that the driving force to make the dispersants adsorb on the particle surface was too weak for redispersion to occur.

As presented in Table 15, most dispersant-toluene combinations resulted in products displaying a three-phase system. All samples in toluene after both shaking and sonication can be seen in Figure 24 below.



Figure 24. REF CC⁵-CAC-2.5 powder in toluene using dispersant A, B, C, D, E, F, G, H, I.

As Figure 24 illustrates, all samples contained a silica sediment and no significant difference can be seen amongst the samples. The sediment heights were approximately the same, but all dispersants except A, E, G and H produced samples displaying this three-phase system with an increased amount of light sediment in toluene. However dispersant D and I resulted in products with the most considerable light sediment-phase.

Both dispersant *D* and *I* are nonionic and are low molecular weight dispersants. They have some chemical similarities, both containing alcohol and ethylene oxide groups, and these factors may all have influenced the dispersant-surface interaction in the solvent system. The diffusion rate of smaller molecules is high, allowing more molecules to reach the surface and the nonionic nature of the dispersant works well with the particle surface as it is not charged. However, as Figure 24 clearly shows no redispersion has occurred.

To investigate whether an increased dispersant to silica ratio could improve the redispersibility of silica, additional samples with a higher dispersant to silica ratio, 2:1 and 3:1, were produced using these two dispersants. These samples along with the reference and the 1:1 ratio samples can be seen after shaking and sonication in Figure 25 A) and B).

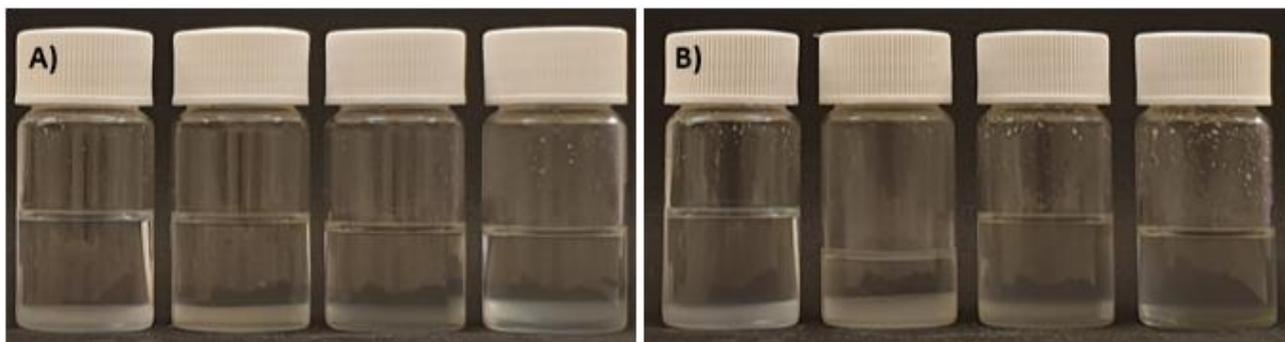


Figure 25. From left to right: A) Ref D 1:1, 2:1 and 3:1 B) Ref I 1:1 2:1 and 3:1.

The sediment heights are approximately the same in all six dispersant samples, where the only distinction is how fast the samples form a sediment upon shaking. The higher dispersant concentrations form a sediment at a lower rate; however, this is more likely due to an increase in viscosity rather than a consequential difference in dispersant-surface interaction as all samples form a similar sediment after some time.

Furthermore, redispersion of the CC⁵-CA-7-SD powder was also examined using *D* and *I* in a dispersant to silica ratio range of 1:1 to 3:1. The CC⁵-CA-7-SD samples can be seen after shaking and sonication in Figure 26 A)-B) along with a reference sample only containing CC⁵-CA-7-SD and toluene.



Figure 26. A) REF CC⁵-CA-7-SD in toluene with 1:1, 2:1, 3:1 D: Silica B) REF CC⁵-CA-7-SD in toluene 1:1, 2:1, 3:1 I: Silica.

All CC⁵-CA-7-SD samples had a lighter and relatively high sediment, however, similar to the CC⁵-CAC-2.5 samples, there are no considerable differences amongst the samples apart from the rate a sediment is formed. As mentioned, the variation in the rate of sedimentation is likely due to an increase in viscosity. Compared to the CC⁵-CAC-2.5 samples, the sediments are considerably lighter, with no compact sediment. Furthermore, this lighter sediment and increase in sediment height is presumably due to the smaller particle size of the spray dried powder. As the sediment in all samples became more compact over time and no sample fully redispersed, the variation in sediment type is likely not a result of a better dispersant-surface interaction in the solvent, but rather a direct result of the smaller particle size of the powder.

The dispersant adsorption was likely small, as all samples were very similar to the reference sample, Consequently, this observation strongly indicates that there are weak dispersant interactions with the particle surface. One explanation to the low silica-dispersant interaction is that the silica surface itself is inactive due to the diols. The diols are meant to reduce surface interaction, which is why the siloxane-bond formation is repressed in the drying step, making redispersion possible. However, there is no force driving the dispersant to interact with the silica particle surface. Due to the inert nature of the surface, the surface-dispersant interaction is absent and redispersion in organic solvents is not possible.

Another explanation is that the redispersion method itself is insufficient, so to further evaluate the redispersibility of silica in toluene, more energy was added to the system by putting both CC⁵-CAC-2.5 and CC⁵-CA-7-SD dispersant *D* and *I* 1:1 (wt:wt) at 70 °C for 24 h followed by 3 min sonication at 20% amplitude.

All samples contained a sediment; however, before the samples cooled to room temperature, the CC⁵-CA-7-SD samples were redispersed, i.e. the samples only contained one, clear phase without a sediment. This strongly indicates that heat plays a crucial role for redispersion of silica in toluene, even though the samples sedimented as its temperature decreased. However, using heat to improve dispersion in organic solvents is complicated for many reasons, such as low boiling points and fire hazards. Hence, using heat for redispersion of silica in organic solvents is difficult and impractical.

4.4.2 Redispersion of Silica with both amine- and diol-covered surface

The redispersibility of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 was investigated in toluene, cyclohexane, ethyl acetate and isopropanol, due to their difference in polarity. Table 16 below describes the reference samples and if and how each sample deviated from its reference.

Table 16. How each dispersant sample deviated from their reference.

CC ^{4.5} -A ^{0.5} -CAC-7.6	Ref	D	F	I
T	LS, CS	>SH	>SH	>SH
CH	LS, CS	>SH	SS	SS
EA	LS, CS	>LS, >SH	>LS, >SH	>LS, >SH
IP	LS, CS	ND	ND	ND
CC ^{4.5} -A ^{0.5} -CA-9.8	Ref	D	F	I
T	LS, CS	>LS, >SH	>LS, >SH	>LS, >SH
CH	LS, CS	>LS, >SH	>LS, >SH	ND
EA	LS, CS	>LS, >SH	>LS, >SH	>CS
IP	LS, CS	ND	ND	ND

ND-No deviation

LS-Light sediment

CP-Compact sediment

V-Viscous

SS-Slow sedimentation

SH-Sediment height

As Table 16 shows, all samples but the ones in isopropanol deviated from the reference, indicating a dispersant-surface interaction. However, in cyclohexane and ethyl acetate the differences were slight, contrary to the toluene samples where a considerable variation from the references was observed. Figure 27 A) and B) below displays all CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 samples in toluene, respectively. Images of CC^{4.5}-A^{0.5}-CAC-7.6 and CC^{4.5}-A^{0.5}-CA-9.8 samples in cyclohexane, ethyl acetate and isopropanol are found in Appendix VII.

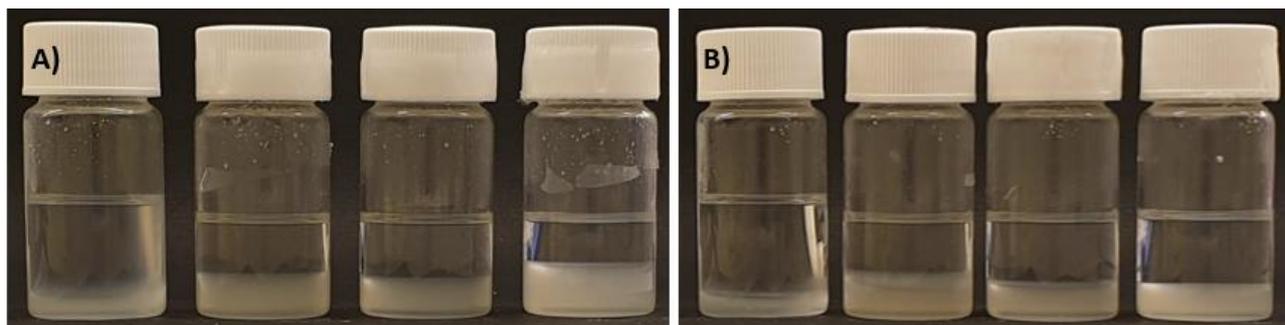


Figure 27. From left to right: A) CC-4.5-A-0.5-CAC-7.6 reference, dispersant F, D, I and B) CC-4.5-A-0.5-CA-9.8 reference, and dispersant F, D, I, both in toluene

Figure 27 illustrates that all dispersant samples significantly differed from their reference. This improvement suggests that there is a dispersant-surface interaction in all cases. Furthermore, both samples series are quite similar despite the rounder, smaller agglomerates of the $CC^{4.5}-A^{0.5}-CA-9.8$ powder. This suggests that surface modification affects redispersion more than agglomerate size. However, the powders also differed in the amount of ions present, where the $CC^{4.5}-A^{0.5}-CA-9.8$ powder had been ion exchanged twice while the $CC^{4.5}-A^{0.5}-CAC-7.6$ had been ion exchanged three times. Hence, ions may have a negative effect on redispersion in organic solvents.

Two of the dispersants, *D* and *I*, are nonionic, while dispersant *F* is anionic. As expected, dispersant *F* seem to interact well with the surface of both the $CC^{4.5}-A^{0.5}-CAC-7.6$ and $CC^{4.5}-A^{0.5}-CA-9.8$ powders, yielding products with very similar sediments. This might be due to an electrostatic interaction with the positively charged amine on the particle surface and the anionic head group of the dispersant. As mentioned earlier, the sample series are similar. However, samples with dispersant *I* resulted in different sediment phases depending on the powder used, where the $CC^{4.5}-A^{0.5}-CAC-7.6$ powder sample had the highest sediment. This could be due to natural variance as only one sample was prepared, and the statistical uncertainty is low.

As mentioned previously, both the CCA-modified powders yielded products with light sediments. The sediments were similar to the $CC^5-CA-7-SD$ samples, which is notable due to the large difference in the particle size of the powders. The lighter sediment indicates that there is a stronger dispersant-surface interaction with the amine on the surface compared to the CC-modified powder where the surface is completely covered in diols.

All samples were also exposed to 70 °C for 24h. A difference in sediment height could be observed while the samples were warm, but after cooling and sonication there were no significant differences before and after the samples had been exposed to heat. Similar to the $CC^5-CAC-2.5$ and $CC^5-CA-7-SD$ samples, this indicates that heat improves the redispersion. However, the samples need to be exposed to an increased temperature or have a longer exposure time in 70 °C. This is not practical mainly due to the long process time.

4.5.3 Adding dispersant prior to drying

Drying silica with dispersants did not improve redispersion in organic solvent. This is clearly seen in Figure 28 below as all samples are sedimented. There is no significant difference when comparing the samples to their references, where the dispersant was added directly to the system instead of prior to drying.

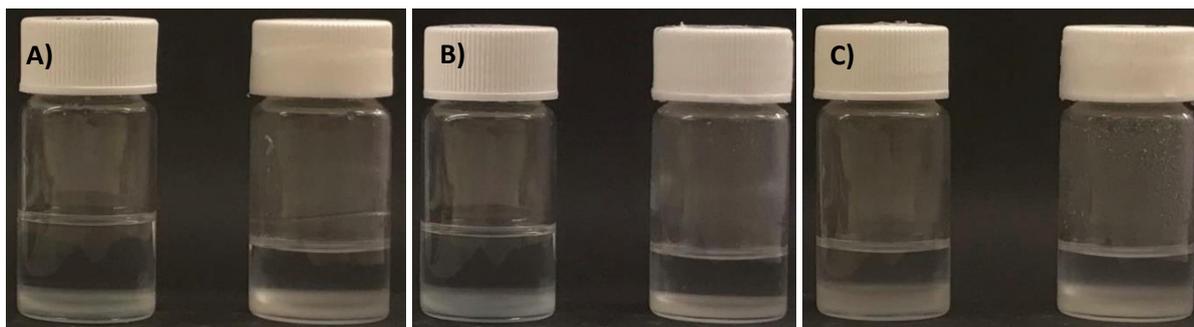


Figure 28. From left to right: Toluene and A) Dispersant B ref, Dispersant B added prior to drying. B) Dispersant E Ref, Dispersant E added prior to drying C) Dispersant I ref, Dispersant I added prior to drying

Adding dispersant prior to drying the colloidal silica results in a powder where dispersants is present between the silica particles, inhibiting direct contact between the silica particles. This could help the redispersion in organic solvents, however, Figure 28 shows that there is no significant difference between the samples where dispersant had been added before drying and the samples where dispersant was added directly to the solvent. Hence, addition of dispersant before drying did not do any substantial difference regarding redispersion.

PEG was also used to try to improve redispersibility, by increasing the wettability of the particle surface, seen in Figure 29. The PEG reference sample consist of only silica and toluene. PEG is advantageous as it is soluble in both water and toluene.



Figure 29. From left to right: CC^5 -CAC-2.5 in toluene, CC^5 -CAC-2.5 dried with PEG present in toluene

As illustrated in Figure 29, addition of PEG did not affect the redispersion or the sediment significantly either.

4.5 Surface modification

A different route was explored as none of the previous attempts to redisperse silica in organic solvent was successful. As no proof of direct surfactant-silica interaction could be demonstrated for the CC-silane surface modified nanoparticle, further surface modification was necessary to promote redispersion and to make the surface more hydrophobic.

4.5.1 Effect of bound water

The comparison between additionally dried silica and non-additionally dried silica in toluene and isocyanates, resulted in samples all displaying a three-phase system containing a clear solvent phase, a milky turbid phase and a sediment phase. The percentage of turbid phase was calculated by taking the height of the turbid phase and dividing it with the total height of the sample. This was a rough approximation as it was difficult to differentiate between the turbid phase and the sediment phase.

Samples containing silica that had been additionally dried showed no improvement regarding the height of the turbid phase. In fact, as seen in Figure 30, the samples containing non additionally dried silica had a turbid phase equal or higher compared to the additionally dried silica after 24 h. The raw data for Figure 30 can be found in Appendix XIII.

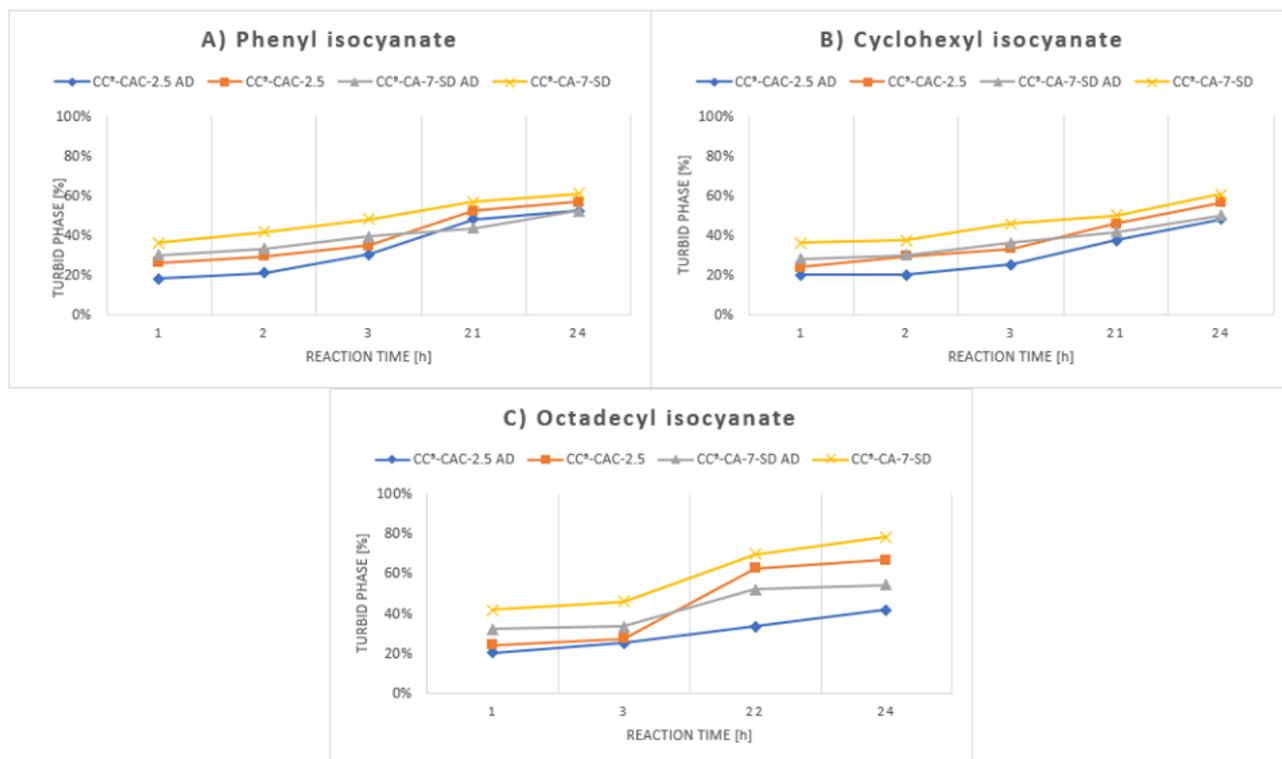


Figure 30. Percentage turbid phase as a function of reaction time in toluene with a) phenyl isocyanate, b) cyclohexyl isocyanate c) octadecyl isocyanate

The silica which was not additionally dried reached a higher percentage of turbid phase and at a higher rate. This suggests that the tightly bound water is acting as a catalyst, accelerating the reaction between the silica and the isocyanate. This effect is seen for all isocyanates in toluene. Hence, no additional drying is necessary to obtain an isocyanate surface modification. Furthermore, after a sufficient reaction time there were no notable differences between the CC⁵-CAC-2.5 and CC⁵-CA-7-SD samples, suggesting that the roughness of the powder can be disregarded when redispersing silica via surface modification.

4.5.2 Surface modification in Toluene

Figure 31 A)-C) is demonstrating the turbid phase percentage in relation to reaction time for each method. The turbid phase data is found in Appendix IX.

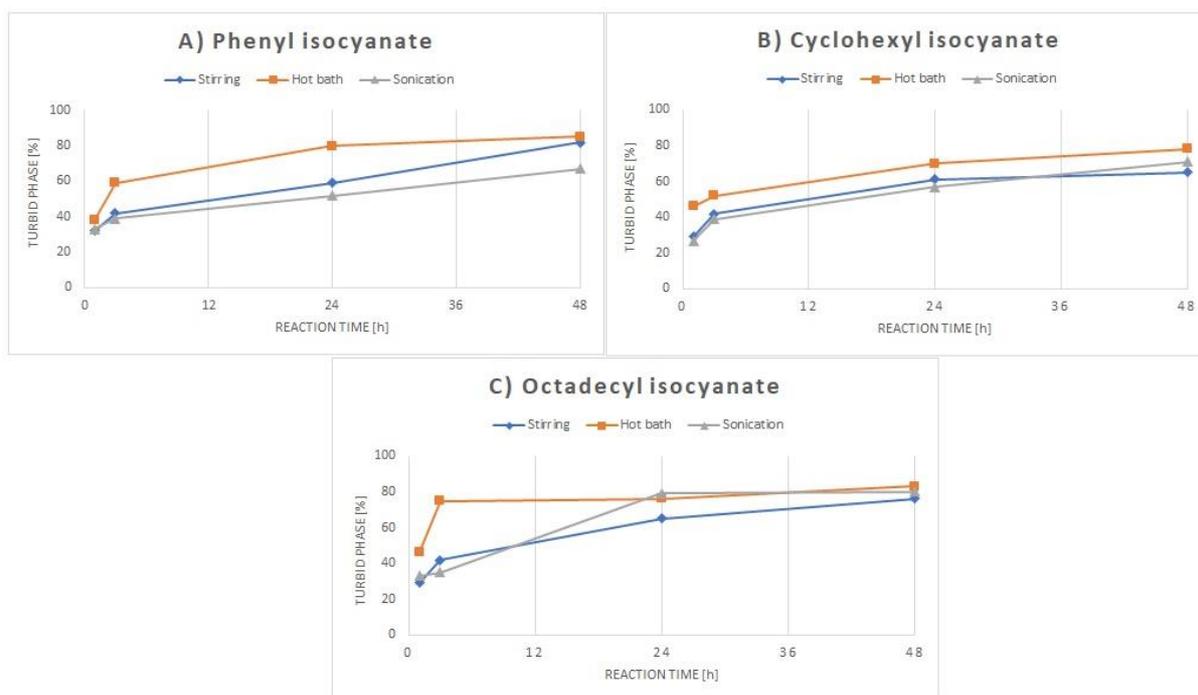


Figure 31. a) Method evaluation with phenyl isocyanate surface modification in toluene b) method evaluation with cyclohexyl isocyanate surface modification in toluene c) method evaluation with octadecyl isocyanate surface modification in toluene.

There is no significant change in the height of the turbid phase between the different methods or type of isocyanate after 48 h. Slight variations may be due to low accuracy during sample preparation. The addition of the isocyanates was done quick to decrease the risk of exposure as the isocyanates are highly reactive. A syringe was used for quick and safe addition of isocyanates. Hence, the volumes added were approximately measured. The calculated turbid phase percentage may also differ as gel accumulated onto the walls after a few hours of reaction due the rapid stirring. Interestingly, gelling was observed during the reaction with isocyanate, supporting the claim that a surface reaction has occurred. High amounts of gel on the vial walls would result in a decreased turbid phase.

Figure 32 is illustrating the comparison of the reaction method of CC⁵-CAC-2.5 silica with phenyl, cyclohexyl and octadecyl surface modification in toluene, after 48 h. As seen below, most samples experience gelling on the walls.



Figure 32. Comparison of the reaction methods stirring, hot bath and sonication for each isocyanate. A) Phenyl isocyanate B) cyclohexyl isocyanate and C) octadecyl isocyanate.

The results seen in Figure 32 imply that the method of choice is not making a significant difference in turbid phase height as all samples reach approximately the same height regardless of method. However, heat seem to be accelerating the reaction as the hot bath method results in the highest turbid phase after 24 h, for all isocyanates. For all octadecyl isocyanate samples, the sonication method reached the same height as hot bath samples after 24 h. However, this is likely due to the elevated temperature in the sonication bath as the

initial temperature in the sonication bath was higher. This was as both phenyl- and cyclohexyl isocyanate samples were run directly prior, heating the bath to a starting temperature of roughly 40 °C instead of 21 °C.

A higher turbid phase resulted in a decreased sediment phase, suggesting that silica is in fact redispersed in the solvent. However, it was problematic to measure the particle size of the redispersed silica. It was not possible to measure the size by DLS as all analyzed samples resulted in inaccurate measurements and errors, stating that the particles had a size greater than possible to measure on the instrument. Hence, the trials to analyze the particle size was interrupted while exploring better alternatives.

4.5.3 Other solvents

The percentage turbid phase present in each sample was plotted against stirring time, displayed in Figure 33 A)-D). The calculated turbid phase percentage along with the raw data is found in Appendix X.

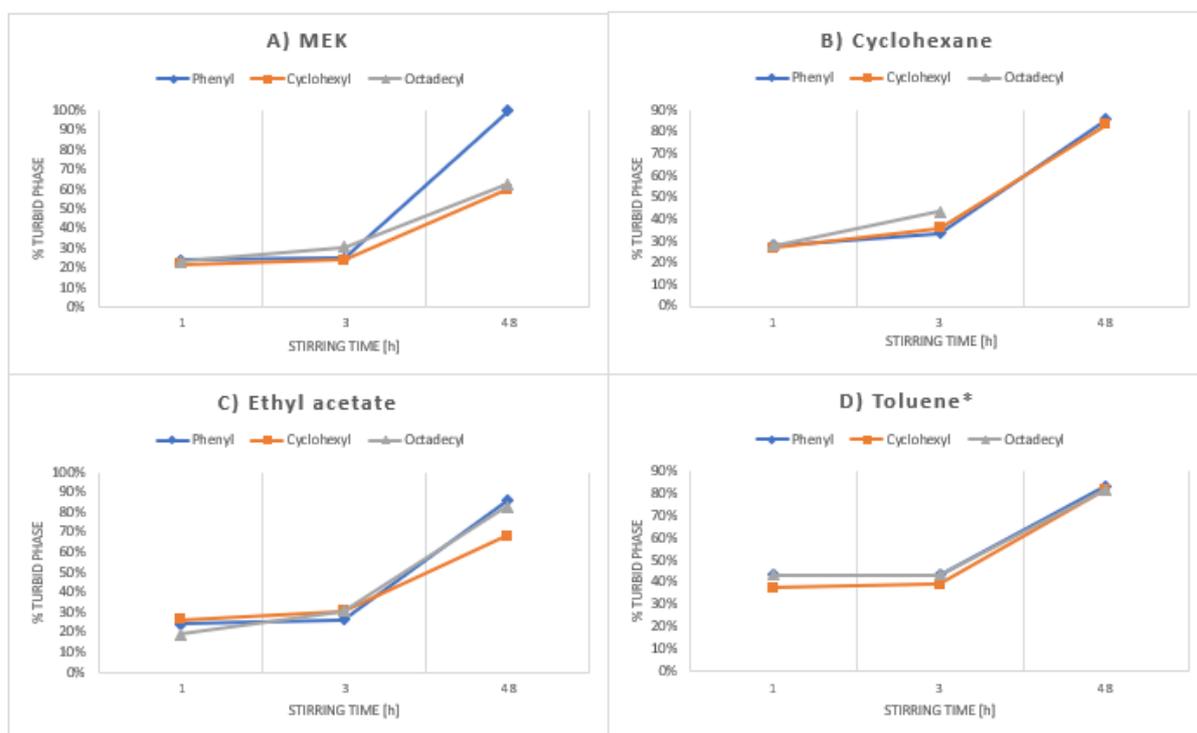


Figure 33. Percentage turbid phase as a function of reaction time in A) MEK B) Cyclohexane C) Ethyl acetate and D) toluene * CC⁵-CA-7-SD powder.

As Figure 33 shows, MEK yielded products with the largest and the smallest turbid phases after 48 h, where the phenyl isocyanate yielded a sample only containing a turbid phase and a small sediment at the bottom. Samples made with cyclohexane as solvent resulted in high amounts of gel after 48 h. The sample with the cyclohexane and octadecyl isocyanate generated so much gel that it was not possible to determine and measure the turbid phase after 48 h. The cyclohexyl isocyanate in ethyl acetate had a slightly smaller turbid phase, 68%, compared to the other samples which were quite similar, with an 82-86% turbid phase.

These differences in turbid phases are likely due to the different reaction medias. The variations amongst all samples in cyclohexane and toluene, as well as the phenyl- and octadecyl isocyanate samples in ethyl acetate, are very small. All these samples have turbid phases in the range of 82-86%, indicating that there is a similar degree of modification and/or similar amounts of silica redispersed.

The octadecyl isocyanate samples in MEK and cyclohexyl isocyanate samples in MEK and ethyl acetate had lower percentages turbid phases, 60-68%, suggesting that these isocyanate-solvent combinations are less

favorable. The phenyl isocyanate in MEK yielded a product with a 100% turbid phase, strongly suggesting that this solvent-isocyanate combination gives the best result.

An FTIR was performed on the CC⁵-CA-7-SD in toluene in order to confirm the covalent bonding of the isocyanates to the hydroxyl groups, seen in Figure 34 below.

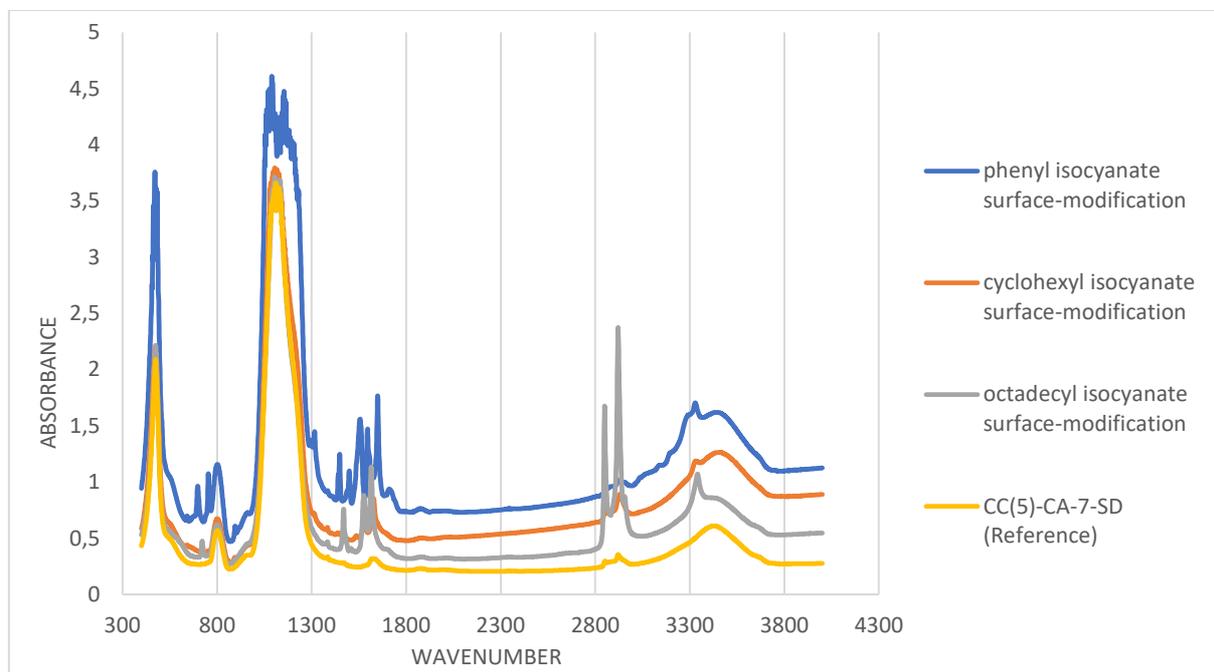


Figure 34. CC⁵-CA-7-SD (Reference), CC⁵-CA-7-SD further surface-modified with phenyl isocyanate, CC⁵-CA-7-SD further surface-modified with cyclohexyl isocyanate and CC⁵-CA-7-SD further surface-modified with octadecyl isocyanate.

As seen in the spectrum, there are peaks at 1500-1700 cm⁻¹ which are absent from the reference. These would correspond to a urethane group; however, none are distinct and sharp which is a characteristic of those types of peaks. Hence, the surface modification could not be confirmed, yet, the gelling and the turbid phase of the samples indicates that some sort of modification has occurred.

To investigate whether the height of the turbid phase was proportional to amount of silica redispersed, the dry content per gram turbid phase was determined. Only CC⁵-CAC-2.5 in MEK, cyclohexane and ethyl acetate and CC⁵-CA-7-SD in toluene was examined, all using the stirring method.

Table 17. Dry content per gram turbid phase for all samples. *CC⁵-CA-7-SD powder was used.

	MEK	CH	EA	T*
Phenyl isocyanate [g dry content/g turbid phase]	0.09	0.13	0.13	0.14
Cyclohexyl isocyanate [g dry content/g turbid phase]	0.14	0.13	0.14	0.10
Octadecyl isocyanate [g dry content/g turbid phase]	0.18	0.14	0.19	0.17

As Table 17 shows, there are differences in dry content, with results spanning 0.09 – 0.19 g dry content/g turbid phase. Phenyl isocyanate in MEK had the lowest dry content, which likely is due to the 100% turbid phase. Furthermore, large differences can be observed between phenyl isocyanate and cyclohexyl isocyanate in toluene. Structurally, these isocyanates are similar, but the phenyl ring in the phenyl isocyanate and toluene may interact through π - π bonding and, as expected, the results indicates that phenyl isocyanate has a better solvent interaction in toluene. However, any strong conclusion cannot be drawn due to low statistical certainty.

Octadecyl has a richer silica content in the turbid phase, as seen in Table 17. This may be due to its higher molecular weight, making it good for steric stabilization. Hence, further surface-modification by high molecular weight isocyanates might be beneficial for redispersion of silica, if a slightly larger particle size is acceptable.

4.6 General discussion

The drying method of the silica sol has affected the redispersion in both aqueous and non-aqueous systems. Spray drying results in a more uniform silica powder with smaller agglomerates. Hence, it is more easily redispersed in aqueous systems due to the larger total surface area and more accessible interaction possibility. Even if rotary evaporation of CC^{4.5}-A^{0.5}-CA-9.8 resulted in smaller round particles, these are not comparable to CC⁵-CA-7-SD as the particle size and size distribution is considerably smaller for the spray dried powder.

The effect of powder particle size is clear when examining the samples in ethylene glycol. CC⁵-CA-7-SD was the only powder that could be redispersed, suggesting that agglomerate size of the powder affect the redispersion more than the surface modifications examined in this study. If surface modification was the only condition for the redispersion, then CC⁵-CAC-2.5, CC⁵-CA-7 and CC⁵-CAC-9 should have redispersed in ethylene glycol as well since all have the same silane surface modification. However, if agglomerate size of the particles was the only factor, the CCA-modified powder samples should have differed more, as the CC^{4.5}-A^{0.5}-CA-9.8 had significantly smaller agglomerates.

Ethylene glycol is the solvent in this study most similar to water in polarity, which is why it was used for redispersion testing without the addition of dispersant. However, there is a notable absence of driving forces for redispersibility in ethylene glycol, compared to water, and the redispersibility of silica is significantly decreased in organic solvents as the driving forces present in water are removed. Salt between the dried silica particles promoted the redispersion in water due to the osmotic force present, as seen when redispersing CC⁵-CAC-9 in water. However, as there is weak osmotic force in organic solvent, the salt is not affecting the redispersion in ethylene glycol. Hence, the lack of driving forces complicates the redispersion of silica in organic solvent.

To overcome the problem of redispersing silica in organic solvent, dispersants were added to the particle-solvent systems. Dispersants should adsorb to the surface through physical bonding and sterically stabilize the particle while increasing the wettability in the solvent. However, the lack of hydrophobic effect in organic solvents leaves electrostatic interactions and van der Waal forces as the only driving force for adsorption, forces which might be too weak for the dispersants to adhere to the particle surface, especially with nonionic dispersant. Furthermore, the CC-silane surface modification seemed to be inert, a claim supported by the serum method. The low driving forces and an inert surface modification made the redispersion in organic solvent impossible, with the only exception of CC⁵-CA-7-SD in ethylene glycol. The claim that the CC-modification rendered the particle surface non-active was supported by the fact that CCA-silane modified powder showed an improvement when adding dispersant compared to reference samples in organic solvent.

The drying method did not affect the redispersion when using dispersants in organic solvent to the same extent as in water. The main differences between the spray dried powder and the rotary evaporated ones seemed to be the rate of sedimentation and how light the sediment is perceived to be, both of which could be explained by the smaller agglomerate size of the powder. However, similarities between the sample series further supports the claim that the CC-silane surface modification is unsuitable for adsorption of dispersants. It could, however, serve as anchoring moiety for further surface ad-hoc modification such as hydrophobization.

Redispersion through surface modification with hydrophobic isocyanates was a possible route for redispersion, where the supposed inactive nature of the CC-covered surface would not be a problem. All isocyanate samples showed immediate improvements with a high turbid phase and a smaller sediment,

implying that further surface modification is the best route for redispersion in organic solvent. It was, however, difficult to measure and characterize the turbid phase as DLS measurements were inconclusive, suggesting a particle size too large for DLS measurements. This could suggest that the isocyanates are reacting with big particle agglomerates. The turbid phase indicates that the agglomerates had been broken apart and decreased in size, but the isocyanate surface modification may not sufficiently be helping breakage of agglomerates into primary particles. The gelling occurring after the addition of isocyanates further supports the claim that a surface reaction has occurred.

5. Conclusion

Dried silane functionalized colloidal silica could be fully redispersed and regain its original particle size in aqueous systems using heat and sonication. Even though pH, drying method and silane modification played a crucial role in how much energy input the system required to redisperse, all samples redispersed with enough treatment steps. For aqueous systems, a powder with salt present redispersed with fewer treatment steps and a correlation between particle size of the powder and energy input needed to redisperse the silica was observed, making spray drying and a high pH sol preferred for redispersion in water. Furthermore, agglomerate size of the powder seems to be critical for redispersion without additives in non-aqueous systems as well; the rougher powders could not be redispersed in ethylene glycol while the spray dried could.

For non-aqueous systems, the surface modification route seems superior for redispersion of dried colloidal silica. The driving forces for dispersants to adsorb to the particle surface were too weak in all solvents and a universal method for redispersion in organic solvents was not found; for redispersion in non-aqueous systems the dispersant and surface modification of the colloidal silica needs to be chosen considering both interaction with the surface and solvent. Contrary to the dispersant route for redispersion, the covalent bonding of isocyanate to the hydroxyl group on the CC-silane was promising, even though no sample fully redispersed.

6. Future work

To further investigate the redispersibility of dried colloidal silica, different surface modifications using other silanes should be examined. For example, pairing a hydrophilic and hydrophobic silane should increase the redispersibility in non-aqueous solvents. Additionally, a more surface-active silane should be investigated and chosen for a specific dispersant to promote dispersant-surface interactions.

The isocyanate route should be further evaluated using different isocyanates as well as variation of concentrations.

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Appendix

Appendix I

Calculation: Monolayer of adsorbed dispersant

M_w dispersant- Approximate molecular weight of dispersant [g/mol]

SA- Specific surface area [m^2/g]

$A_{adsorbed\ dispersant}$ Area of adsorbed dispersant [m^2]

N-Avogadro's number

C- dispersant concentration needed for an adsorbed monolayer dispersant per gram silica [mg dispersant/g silica]

$$C = M_w\ surfactant \times \frac{A_{Adsorbed\ surfactant}}{SA} \times \frac{1}{N} \times 1000$$
$$= 400 \times \frac{130}{100 * 10^{-20}} \times \frac{1}{6.022 \times 10^{23}} \times 1000 = 86.35 \frac{mg\ dispersant}{g\ silica}$$

Calculation: Isocyanate coverage

SA- Specific surface area [m^2/g]

cov- Silane coverage [$\mu mol/m^2$]

M_w isocyanate= molecular weight of isocyanate [g/mol]

N-Avogadro's number

m_{SiO_2} - mass powder

$\rho_{isocyanate}$ =density of isocyanate [g/mL]

$V_{isocyanate}$ =volume isocyanate [mL]

ratio: the isocyanate:silica ratio. 1:1 means that one hydroxyl group on each diol reaction

Assuming one hydroxyl group on each diol reacts

$$V_{isocyanate} = \frac{SA \times cov \times 10^{-6}}{M_w\ isocyanate \times \rho_{isocyanate}} \times m_{SiO_2} \times ratio$$

Appendix II

TGA: CC⁵-CAC-2.5

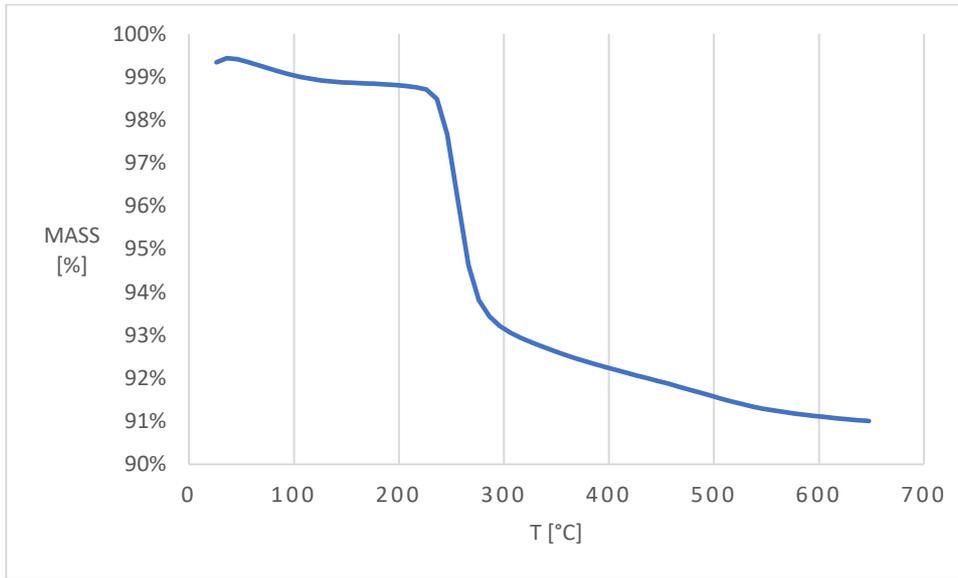


Figure 1. TGA of CC⁵-CAC-2.5. The powder contains approximately 1 wt.% tightly bound water.

TGA: CC⁵-CA-7-SD

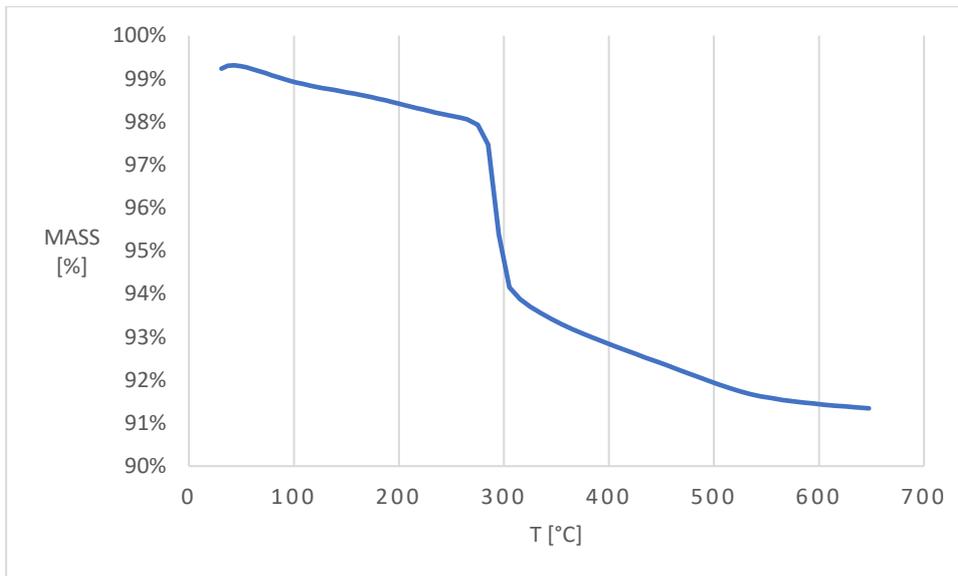


Figure 2. TGA of CC⁵-CA-7-SD. The powder contains approximately 1 wt.% tightly bound water.

TGA: $CC^{4.5}A^{0.5}$ -CA-9.8

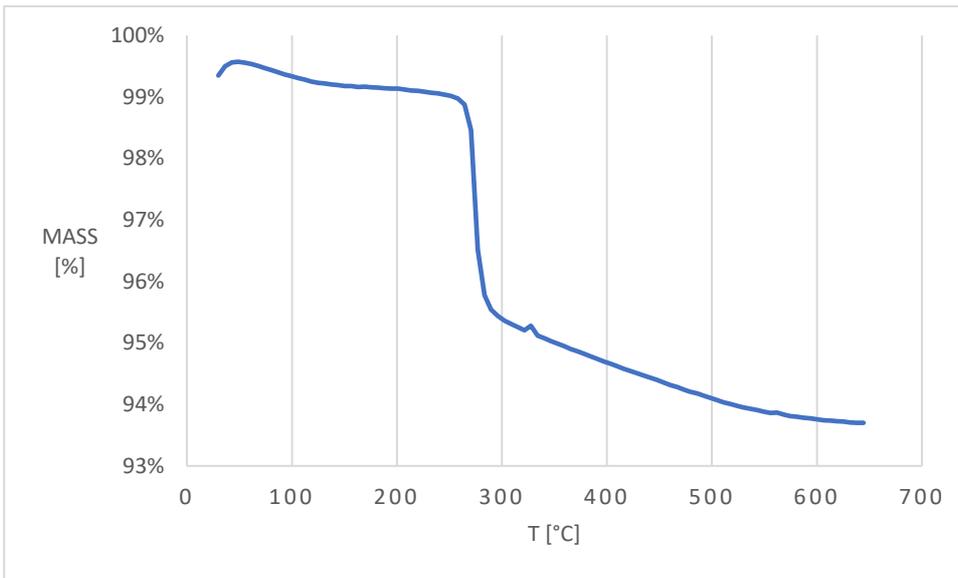


Figure 3. TGA of $CC^{4.5}A^{0.5}$ -CA-9.8. The powder contains approximately 0.5 wt.% tightly bound water.

TGA: $CC^{4.5}A^{0.5}$ -CAC-7.6

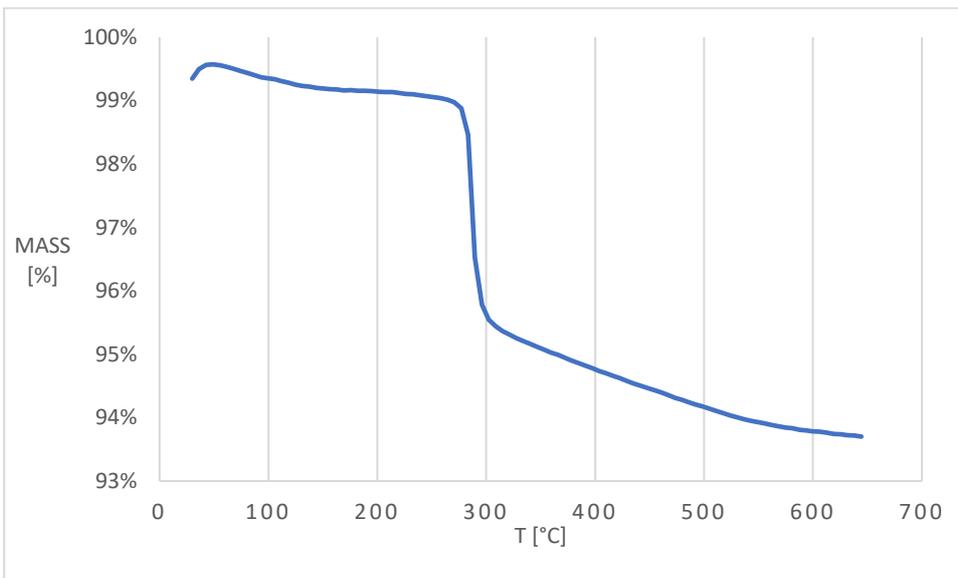


Figure 4. TGA of $CC^{4.5}A^{0.5}$ -CAC-7.6. The powder contains approximately 0.5 wt.% tightly bound water.

Appendix III

Ball milling: CC⁵-CAC-2.5

Table I. Ball milled CC⁵-CAC-2.5 redispersed in MilliQ water by 90 °C oven and 3 min sonication 20 %.

CC⁵-CAC-2.5	90 °C + sonication
Time [h]	DLS [nm]
0	53.7
2	54.6
4	56.5
6	55.4
12	54.2

Ball milling: CC⁵-CA-7

Table II. Ball milled CC⁵-CA-7 redispersed in MilliQ water by 90 °C oven and 3 min sonication 20 %.

CC⁵-CA-7	90 °C	90 °C + sonication
Time [h]	DLS [nm]	DLS [nm]
0	119.0	63.7
2	97.5	51.8
4	105.8	54.8
6	99.3	56.3
12	105.4	53.3

Ball milling: CC⁵-CAC-9

Table III. Ball milled CC⁵-CAC-9 redispersed in MilliQ water by 90 °C oven and 3 min sonication 20 %.

CC⁵-CAC-9	90 °C	90 °C + sonication
Time [h]	DLS [nm]	DLS [nm]
0	46.4	44.5
2	45.3	40.0
4	46.9	42.5
6	46.9	42.9
12	46.8	42.9

Appendix IV

Redispersion without additives: CC-modified silica

Table IV. Particle size of CC-modified silica redispersed in MilliQ water.

	Process 1	Process 2	Process 3	Process 4
Sample	Particle size [nm]	Particle size [nm]	Particle size [nm]	Particle size [nm]
CC ⁵ -CA-7-SD	38.1	36.4	34.0	34.8
CC ⁵ -CAC-2.5	-	53.8	43.8	40.3
CC ⁵ -CA-7	-	58.1	44.1	40.6
CC ⁵ -CAC-9	45.7	39.9	36.9	35.1
	Process 5	Process 6	Process 7	Process 8
Sample	Particle size [nm]	Particle size [nm]	Particle size [nm]	Particle size [nm]
CC ⁵ -CA-7-SD	33.2	32.8	32.8	-
CC ⁵ -CAC-2.5	40.3	40.5	35.9	35.3
CC ⁵ -CA-7	37.8	37.5	36.8	34.4
CC ⁵ -CAC-9	34.8	36.9	35.5	34.5

Redispersion without additives: CCA-modified silica

Table V. Particle size of CCA-modified silica redispersed in MilliQ water.

	Process 1	Process 2	Process 3	Process 4	Process 5
Sample	Particle size [nm]				
CC ^{4.5} A ^{0.5} -CA-9.8	-	63.0	45.7	42.7	38.1
CC ^{4.5} A ^{0.5} -CAC-7.6	56.0	47.6	46.9	41.4	-

Appendix V

Redispersion without additives: Redispersion in ethylene glycol

Table VI. Particle size of CC⁵-CA-7-SD redispersed in ethylene glycol.

	Process 1	Process 2	Process 3	Process 4	Process 5
Sample	Particle size [nm]				
CC ⁵ -CA-7-SD	111.6	85.7	98.8	91.8	91.8

Appendix VI

Ethylene glycol



Figure 5. Reference, ethylene glycol + dispersant B, ethylene glycol + dispersant C, ethylene glycol + dispersant D, ethylene glycol + dispersant E, ethylene glycol + dispersant G and ethylene glycol + dispersant I.

Ethanol

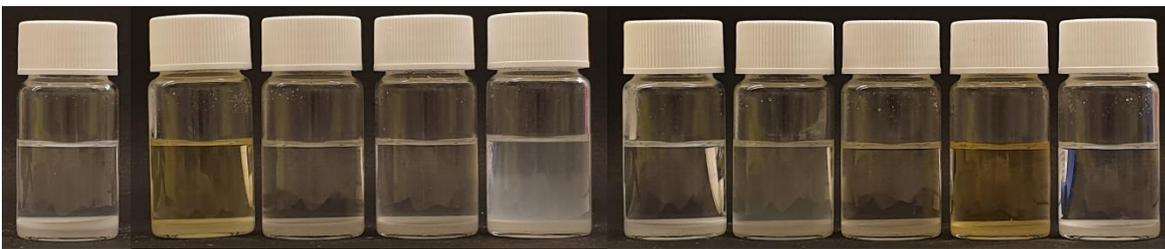


Figure 6. Reference, ethanol + dispersant A, ethanol + dispersant B, ethanol + dispersant C, ethanol + dispersant D, ethanol + dispersant E, ethanol + dispersant F, ethanol + dispersant G, ethanol + dispersant H and ethanol + dispersant I.

Isopropanol

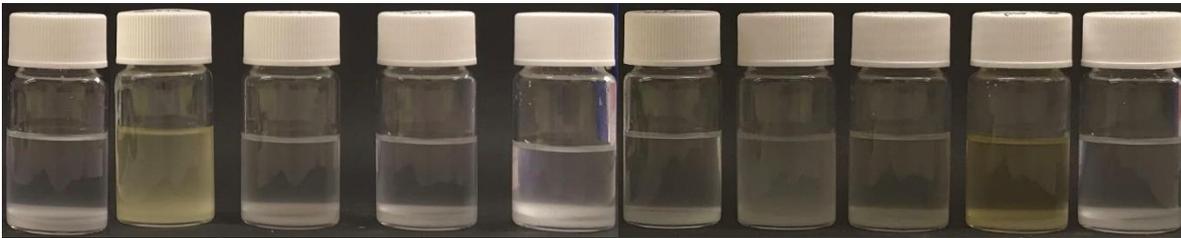


Figure 7. Reference, isopropanol + dispersant A, isopropanol + dispersant B, isopropanol + dispersant C, isopropanol + dispersant D, isopropanol + dispersant E, isopropanol + dispersant F, isopropanol + dispersant G, isopropanol + dispersant H and isopropanol + dispersant I.

Butyl acetate



Figure 8. Reference, butyl acetate + dispersant A, butyl acetate + dispersant B, butyl acetate + dispersant C, butyl acetate + dispersant D, butyl acetate + dispersant E, butyl acetate + dispersant F, butyl acetate + dispersant G, butyl acetate + dispersant H and butyl acetate + dispersant I.

Ethyl acetate

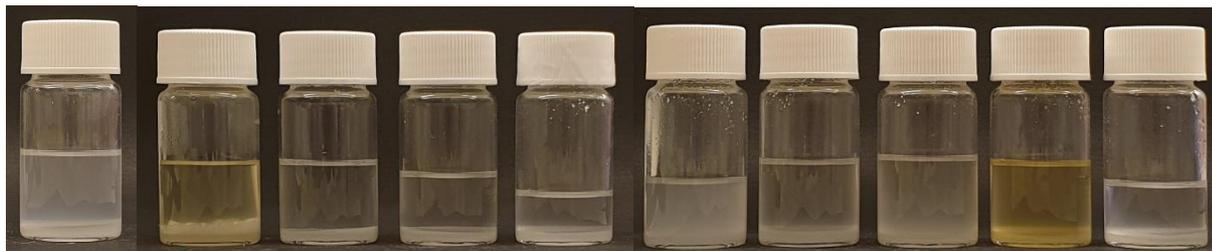


Figure 9. Reference, ethyl acetate + dispersant A, ethyl acetate + dispersant B, ethyl acetate + dispersant C, ethyl acetate + dispersant D, ethyl acetate + dispersant E, ethyl acetate + dispersant F, ethyl acetate + dispersant G, ethyl acetate + dispersant H and ethyl acetate + dispersant I.

MEK



Figure 10. Reference, MEK + dispersant A, MEK + dispersant B, MEK + dispersant C, MEK + dispersant D, MEK + dispersant E, MEK + dispersant F, MEK + dispersant G, MEK + dispersant H and MEK + dispersant I.

Cyclohexane



Figure 11. Reference, cyclohexane + dispersant A, cyclohexane + dispersant B, cyclohexane + dispersant C, cyclohexane + dispersant D, cyclohexane + dispersant E, cyclohexane + dispersant F, cyclohexane + dispersant G, cyclohexane + dispersant H and cyclohexane + dispersant I.

Appendix VII

Cyclohexane



Figure 12. Reference, $CC^{4.5}A^{0.5}$ -CA-9.8 + cyclohexane + dispersant F, $CC^{4.5}A^{0.5}$ -CA-9.8 + cyclohexane + dispersant D and $CC^{4.5}A^{0.5}$ -CA-9.8 + cyclohexane + dispersant I.



Figure 13. Reference, $CC^{4.5}A^{0.5}$ -CAC-7.6 + cyclohexane + dispersant F, $CC^{4.5}A^{0.5}$ -CAC-7.6 + cyclohexane + dispersant D and $CC^{4.5}A^{0.5}$ -CAC-7.6 + cyclohexane + dispersant I.

Ethyl acetate



Figure 14. Reference, $CC^{4.5}A^{0.5}$ -CA-9.8 + ethyl acetate + dispersant F, $CC^{4.5}A^{0.5}$ -CA-9.8 + ethyl acetate + dispersant D and $CC^{4.5}A^{0.5}$ -CA-9.8 + ethyl acetate + dispersant I.



Figure 15. Reference, $CC^{4.5}A^{0.5}$ -CAC-7.6 + ethyl acetate + dispersant F, $CC^{4.5}A^{0.5}$ -CAC-7.6 + ethyl acetate + dispersant D and $CC^{4.5}A^{0.5}$ -CAC-7.6 + ethyl acetate + dispersant I.

Isopropanol



Figure 16. Reference, $CC^{4.5}A^{0.5}$ -CA-9.8 + isopropanol + dispersant F, $CC^{4.5}A^{0.5}$ -CA-9.8 + isopropanol + dispersant D and $CC^{4.5}A^{0.5}$ -CA-9.8 + isopropanol + dispersant I.



Figure 17. Reference, $CC^{4.5}A^{0.5}$ -CAC-7.6 + isopropanol + dispersant F, $CC^{4.5}A^{0.5}$ -CAC-7.6 + isopropanol + dispersant D and $CC^{4.5}A^{0.5}$ -CAC-7.6 + isopropanol + dispersant I.

Appendix VIII

Effect of bound water

Table VII. Effect of tightly bound water

Phenyl isocyanate

	<i>CC⁵-CAC-2.5 AD</i>	<i>CC⁵-CAC-2.5</i>	<i>CC⁵-CA-7-SD AD</i>	<i>CC⁵-CA-7-SD</i>
Time [h]	Turbid phase	Turbid phase	Turbid phase	Turbid phase
1	18%	26%	30%	36%
2	21%	29%	33%	42%
3	30%	35%	39%	48%
21	48%	52%	43%	57%
24	52%	57%	52%	61%

Cyclohexyl isocyanate

	<i>CC⁵-CAC-2.5 AD</i>	<i>CC⁵-CAC-2.5</i>	<i>CC⁵-CA-7-SD AD</i>	<i>CC⁵-CA-7-SD</i>
Time [h]	Turbid phase	Turbid phase	Turbid phase	Turbid phase
1	20%	24%	28%	36%
2	20%	29%	30%	38%
3	25%	33%	36%	46%
21	38%	46%	42%	50%
24	48%	56%	50%	60%

Octadecyl isocyanate

	<i>CC⁵-CAC-2.5 AD</i>	<i>CC⁵-CAC-2.5</i>	<i>CC⁵-CA-7-SD AD</i>	<i>CC⁵-CA-7-SD</i>
Time [h]	Turbid phase	Turbid phase	Turbid phase	Turbid phase
1	20%	24%	32%	42%
3	25%	27%	33%	46%
22	33%	63%	52%	70%
24	42%	67%	54%	78%

Appendix IX

Surface modification in toluene: Stirring

Table VIII. Evaluation of stirring as a reaction method.

	Stirring		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	32	29	29
3	42	42	42
24	59	61	65
48	82	65	76

Surface modification in toluene: Sonication

Table IX. Evaluation of sonication as a reaction method.

	Sonication		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	33	27	33
3	39	39	35
24	52	57	79
48	67	71	80

Surface modification in toluene: Hot bath

Table X. Evaluation of hot bath as a reaction method.

	Hot bath		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	38	46	46
3	59	52	75
24	80	70	76
48	85	78	83

Appendix X

Evaluation of solvents for isocyanate surface-modification: toluene + CC⁵-CA-7-SD

Table XII. Further surface-modification of CC⁵-CA-7-SD in Toluene.

	Toluene + CC⁵-CA-7-SD		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	43	38	43
3	43	39	43
48	83	82	82
72	87	70	77

Evaluation of solvents for isocyanate surface-modification: cyclohexane + CC⁵-CAC-2.5

Tabell XII. Further surface-modification of CC⁵-CAC-2.5 in cyclohexane.

	Cyclohexane + CC⁵-CAC-2.5		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	28	27	28
3	33	36	43
48	86	83	-
72	56	79	-

Evaluation of solvents for isocyanate surface-modification: MEK + CC⁵-CAC-2.5

Tabell XIII. Further surface-modification of CC⁵-CAC-2.5 in MEK.

	MEK + CC⁵-CAC-2.5		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	24	22	23
3	25	24	30
48	100	60	63
72	100	58	60

Evaluation of solvents for isocyanate surface-modification: ethyl acetate + CC⁵-CAC-2.5

Tabell XIX. Further surface-modification of CC⁵-CAC-2.5 in ethyl acetate.

	Ethyl acetate + CC⁵-CAC-2.5		
	Turbid phase [%]		
Reaction time [h]	phenyl	cyclohexyl	octadecyl
1	24	26	19
3	26	30	30
48	86	68	83
72	80	71	71