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Regular Article The silanol content and *in vitro* cytolytic activity of flame-made silica



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ABSTRACT

Hypothesis: The surface chemistry of synthetic amorphous silicas is essential for their applicational performance and for understanding their interactions with biological matter. Synthesis of silica by flame spray pyrolysis (FSP) allows to control the content and type of hydroxyl groups which also affects the cytolytic activity.

Experiments: By controlling the FSP process variables, silica nanoparticles with the same specific surface area but different surface chemistry and content of internal silanols are prepared by combustion of hexamethyldisiloxane sprays, as characterized by Raman and infrared spectroscopy, thermogravimetric analysis, and titration with lithium alanate. Cytolytic activity is assessed in terms of membrane damage in human blood monocytes *in vitro*.

Findings: Unlike commercial fumed silica, FSP-made silicas contain a significant amount of internal silanol groups and a high surface hydroxyl density, up to ~8 OH/nm², similar to silicas made by wetchemistry. Increasing the residence time of particles at high temperature during their synthesis reduces the internal and surface hydroxyl content and increases the relative amount of isolated silanols. This suggests incomplete oxidation of the silica matrix especially in short and "cold" flames and indicates that the silica particle formation pathway involves Si(OH)₄. The surface chemistry differences translate into lower cytolytic activity for "cold-" than "hot-flame" silicas.

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Nomenclature			
Abbreviations DRIFT diffuse reflectance infr FSP flame spray pyrolysis HMDSO hexamethyldisiloxane LDH lactate dehydrogenase MS mass spectroscopy ROS reactive oxygen specie SEM scanning electron mic TEOS tetraethylorthosilicate TGA thermogravimetric and TEM transmission electron	rared Fourier transform rs roscopy alysis microscopy	M n N _A H _c P P R SSA T V	molar mass, kg mol ⁻¹ inlet molar flow rate, mol s ⁻¹ Avogadro's constant, mol ⁻¹ specific combustion enthalpy, J mol ⁻¹ FSP combustion enthalpy feed rate, J s ⁻¹ pressure, Pa reference pressure, Pa precursor solution feed rate, m ³ s ⁻¹ ideal gas constant, J mol ⁻¹ K ⁻¹ specific surface area, m ² kg ⁻¹ temperature, K volume, m ³
dm,modemode hydrodynamic cd_{SSA}specific surface area ecter, mter, mDdispersion oxygen feedggravitational acceleratmmass, kgminlet mass flow rate, k	liameter, m quivalent primary particle diame- 1 rate, m ³ s ⁻¹ ion, m s ⁻² g s ⁻¹	Greek let ρ _p Subscript tot in	ters particle density, kg m ⁻³ 's total inlet

1. Introduction

The properties of synthetic amorphous silicas largely depend on their surface chemistry [1]. This not only determines their application as reinforcing agents in elastomers and rheological additives or flow aids in food and cosmetics, to name a few [2], but can also influence their interaction with biological systems and thus their potential cytotoxicity, as discussed in early [3,4] and recent [5,6] studies. Silanol or hydroxyl (Si—OH) groups are the main determinants of the silica surface chemistry [7] acting as sites for covalent binding of desired species or for hydrogen-bonding with diverse surrounding molecules [3], including water [1]. Surface silanols are classified primarily as hydrogen-bonded (with each other due to their spatial proximity), free isolated and free geminal, the latter referring to two OH groups on the same Si atom [8]. Silanols can be also present inside the silica matrix [1,7] or in ultramicropores (<1 nm) [8] and are then classified as "internal".

The silanol content of synthetic amorphous silicas decreases in a mostly reversible manner with increasing temperature as hydroxyl groups condense into siloxane bridges (\equiv Si-O-Si \equiv) [1,7] and thus it varies with the temperature of production [7,9] as well as application. For instance, pyrogenic or "fumed" silicas that are manufactured industrially by oxidation of chlorosilanes (e.g. SiCl₄ vapor) in high temperature flames typically exhibit rather low surface silanol densities of 2–3 OH/nm^2 [2,7,9] while up to ~8 OH/nm² have been reported for precipitated silicas and gels [10], in fair agreement with a recent computational study suggesting 7.2 OH/ nm² as maximum surface coverage [11]. These findings challenge Zhuravlev's [8] proposal of 4.9 OH/nm² (arithmetic mean, range 4.2-5.7 OH/nm²) as maximum surface silanol content, obtained by investigating >100 different fully hydroxylated amorphous silica samples with the deuterium exchange method that is only sensitive to surface (and not internal) hydroxyl groups.

Much higher silanol contents reported for wet-made silicas (*e.g.* 10–14 OH/nm² [12–13]) have been attributed to the contribution of both surface and internal silanols to the measurement [10]. Internal hydroxyl groups are typically observed in precipitated silicas and gels [7]. Iler [1] considered their presence also in fumed silicas, whereas Barthel et al. [2] did not find any evidence.

Recently, a total silanol content of \sim 13 OH/nm² was determined by infrared spectroscopy for a fumed silica produced by flame spray pyrolysis (FSP) [5]. This approximately five times higher content compared to commercial fumed silicas made with the chloride process was attributed to different chemical reactions of organosilicon precursors in methane/oxygen FSP flames and chlorosilanes in hydrogen/oxygen flames.

Most importantly from a physiological point of view, fumed silicas induce cytotoxic effects at lower concentrations than wetmade Stöber [14] or precipitated [15–16] silicas. Such differences have been attributed partly to a higher proportion of isolated vs. hydrogen-bonded silanols [14] and lower affinity to water [15] of fumed silica that could lead to stronger hydrogen-bonding and/or electrostatic interactions with cell membrane components [17], such as phospholipids [3,6] and proteins [4,18]. On the contrary, when comparing pure to Al- or Ti-doped silicas produced by FSP, alleviation of adverse biological effects with decreasing total silanol content was observed [5]. Furthermore, upon thermal treatment and rehydration of fumed and wet-made silica, no clear correlation between the changes in their total silanol content and their cytotoxicity (if any) could be concluded [14]. On the other hand, Pandurangi et al. [19] reported that decreasing the isolated silanol content of fumed silica by thermal treatment reduced its hemolytic activity. While it is evident that thermal processing of amorphous silicas (either during or after production) influences their silanol content, the relative proportion of isolated vs. hydrogen-bonded silanols and the amount of physisorbed water, the effect of these properties on the biological activity of such silicas is not fully understood and seems highly dependent on the biological system.

Here, the surface and internal silanol content of silicas produced by FSP is quantified by thermogravimetric analysis and titration with lithium alanate, supported by Raman and infrared spectroscopy. It is shown how process conditions and flame enthalpy control the content/type of silanol groups, allowing production of silica nanopowders with comparable specific surface area but distinctly different surface chemistry. This enables studying the relationship between silica hydroxyl content/type and *in vitro* cytolytic activity independent of specific surface area by measuring the Download English Version:

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