Development of the particle and pore structure of silica below the isoelectric point

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Current production of nano-silica

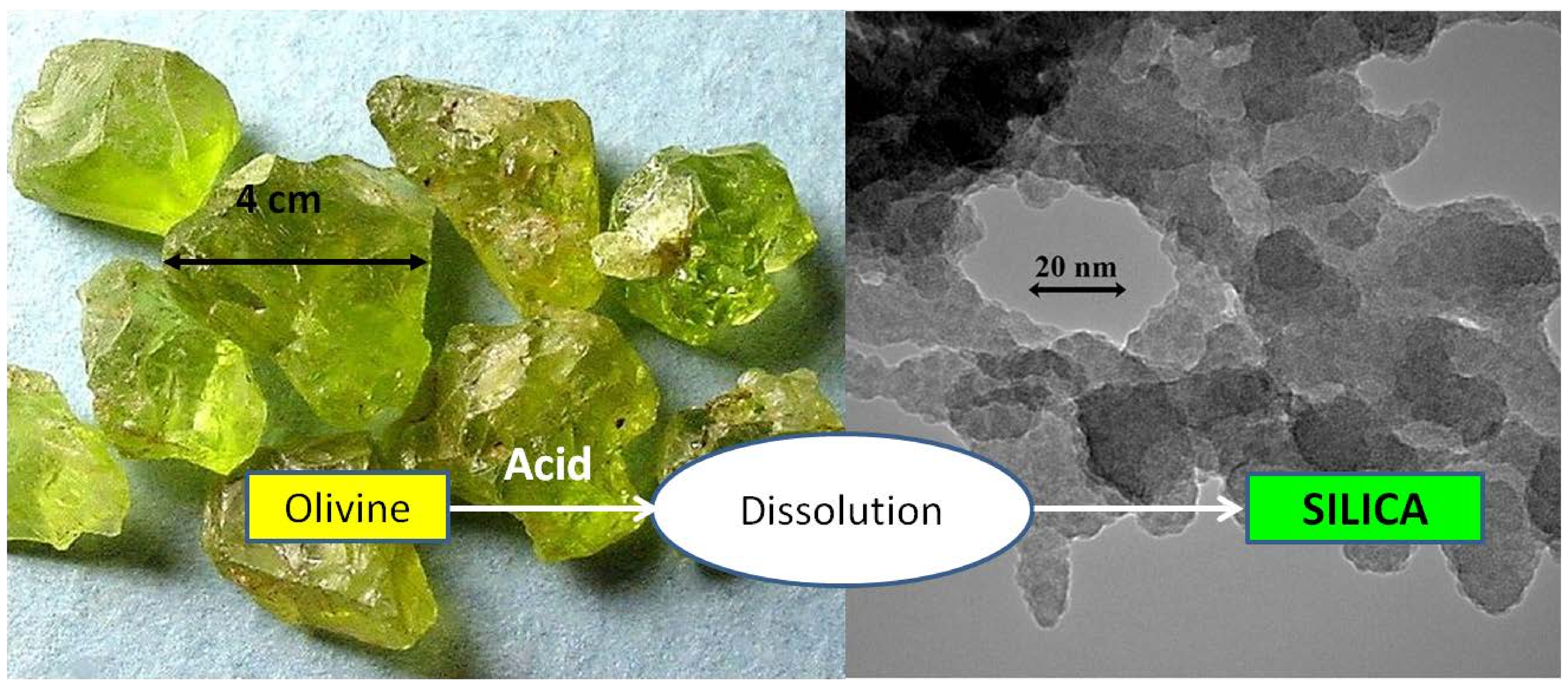
Nano-silica is one of the compounds that is boosting the field of nano-materials with an annual rise of 5.6 % reaching 2.8 million metric tons in 2016 and with a total value of \$6.4 billion [1]. The current production methods involve steps with high temperatures. To reach these temperatures huge amounts of fuel are consumed making these processes: a) **non-sustainable** because of the scarcity of fuels; b) not environmentally friendly because of the huge amount of CO_2 emissions released; and c) expensive because of the fuel price.

Production of olivine nano-silica

Initial research has demonstrated that nano-silica can be produced by dissolving olivine in acid at ***low temperatures***. The acid is neutralized by olivine mineral, according to:

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2(Mg,Fe)^{2+}$$

The neutralization yields a slurry consisting of magnesium/iron salts, silica and unreacted silicates (more details in [2, 3, 4]).



Featured article and cover of the Chemical Engineering Journal [2]: *The properties of amorphous nano-silica synthesized by the dissolution of olivine.*

Experimental Methods

Nano-silicas prepared via the olivine route were analyzed to determine their **pore structure and specific surface area** (SSA) using the nitrogen physisorption, NMR and PALS (positron annihilation lifetime spectroscopy) techniques.

Results

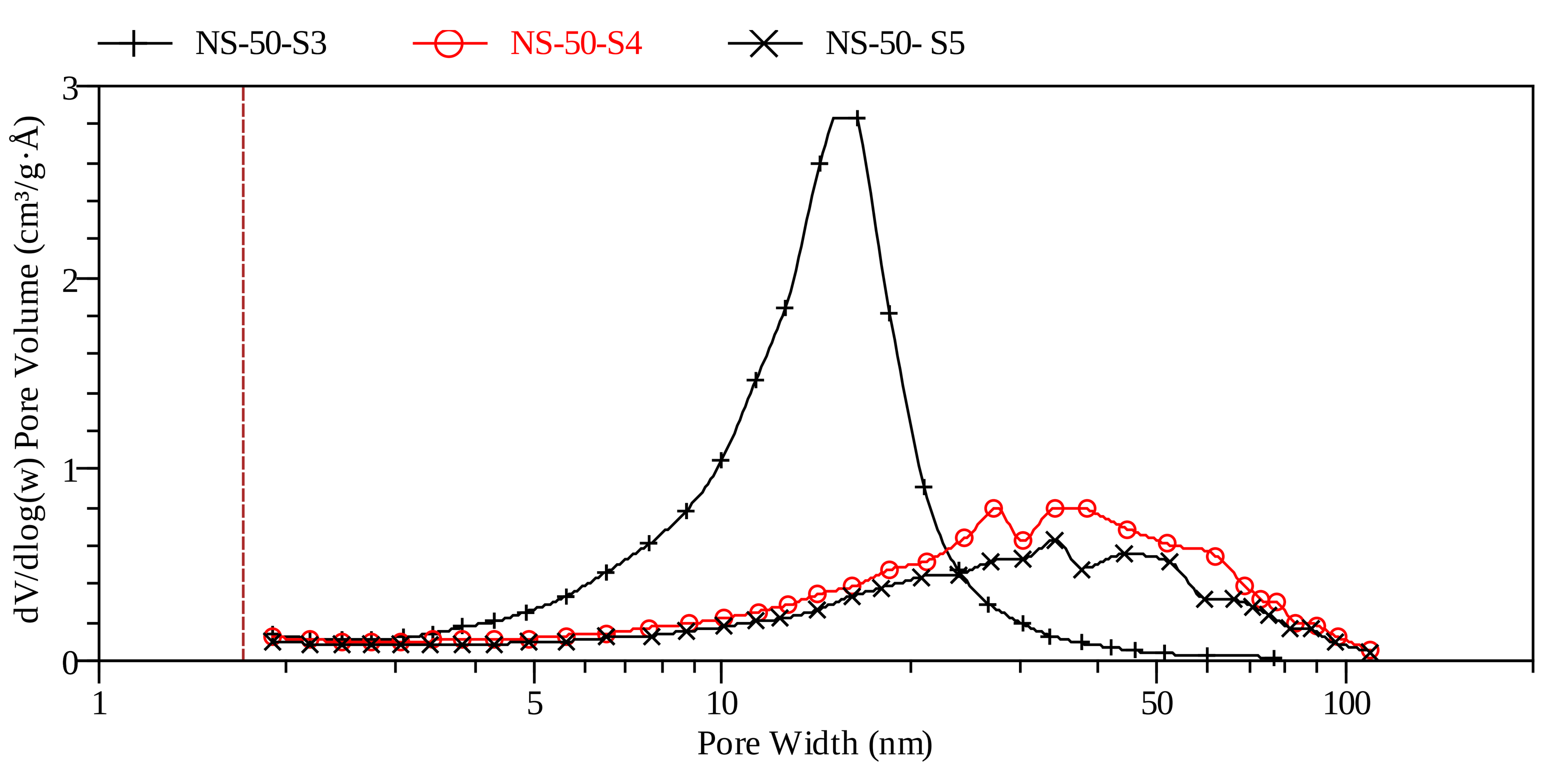


Figure 1. Pore size distribution (PoSD) determined by the BJH method of olivine nano-silica at different reaction times (X=38, 77 and 90 %).

Olivine nano-silica exhibits a SSA_{BET} in the range of 100 to 500 m^2/g. The PoSD is in the range of 2 to 100 nm being affected by the process conditions.

The silanol number is in the range of 13 to 22 OH/nm^2. These high silanol values are due to the presence of internal and ultramicropore silanols. In the PALS analyses two types of pores were found, one at around 6 Å and another one at around 25 Å.

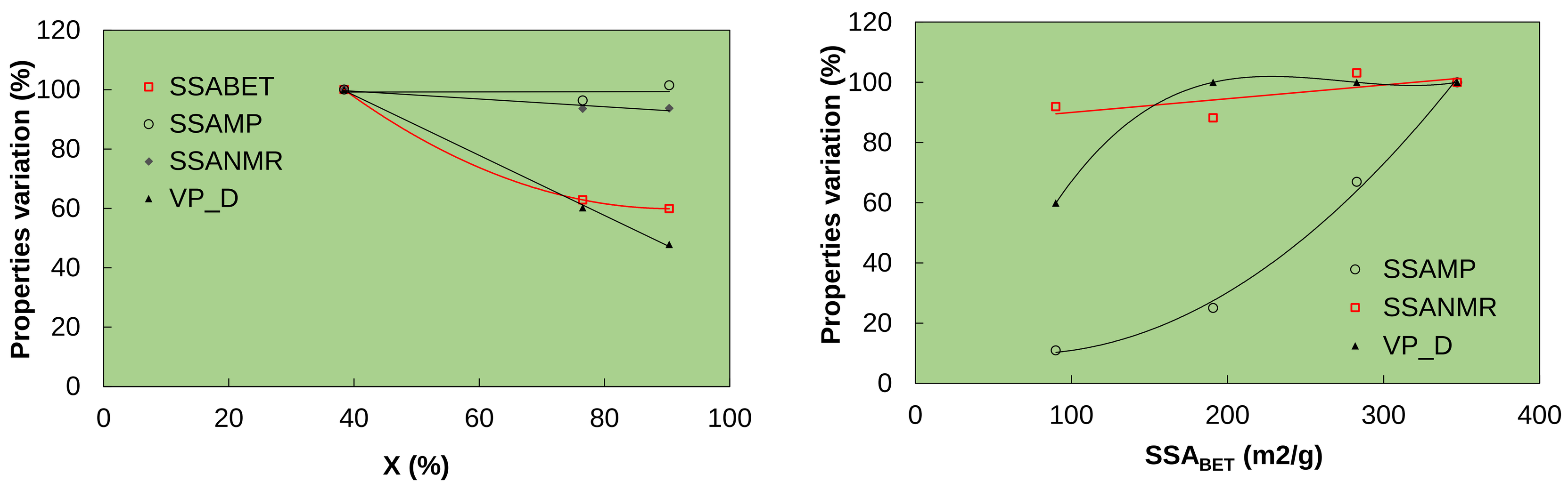


Figure 3. Variation of different properties of silica (SSA_{BET}, SSA_{MP}, SSA_{NMR}, and V_{P_D}) with the reaction conversion and the SSA_{BET}.

The development of the nano-silica structure during the olivine process can be described by the following steps: 1) initially, soluble silica nucleates and primary particles of around 2 nm are formed; 2) the silica particles grow via a condensation route, forming linear chains; 3) as the growth continues, the silica particles keep increasing in size, resulting in 3D networks; and 4) with time, the aggregates become larger and more compact. The final result is agglomerates as big as 20 μm. In addition, internal pores are developed with the conversion degree as the result of condensation of two blocks of silica particles.

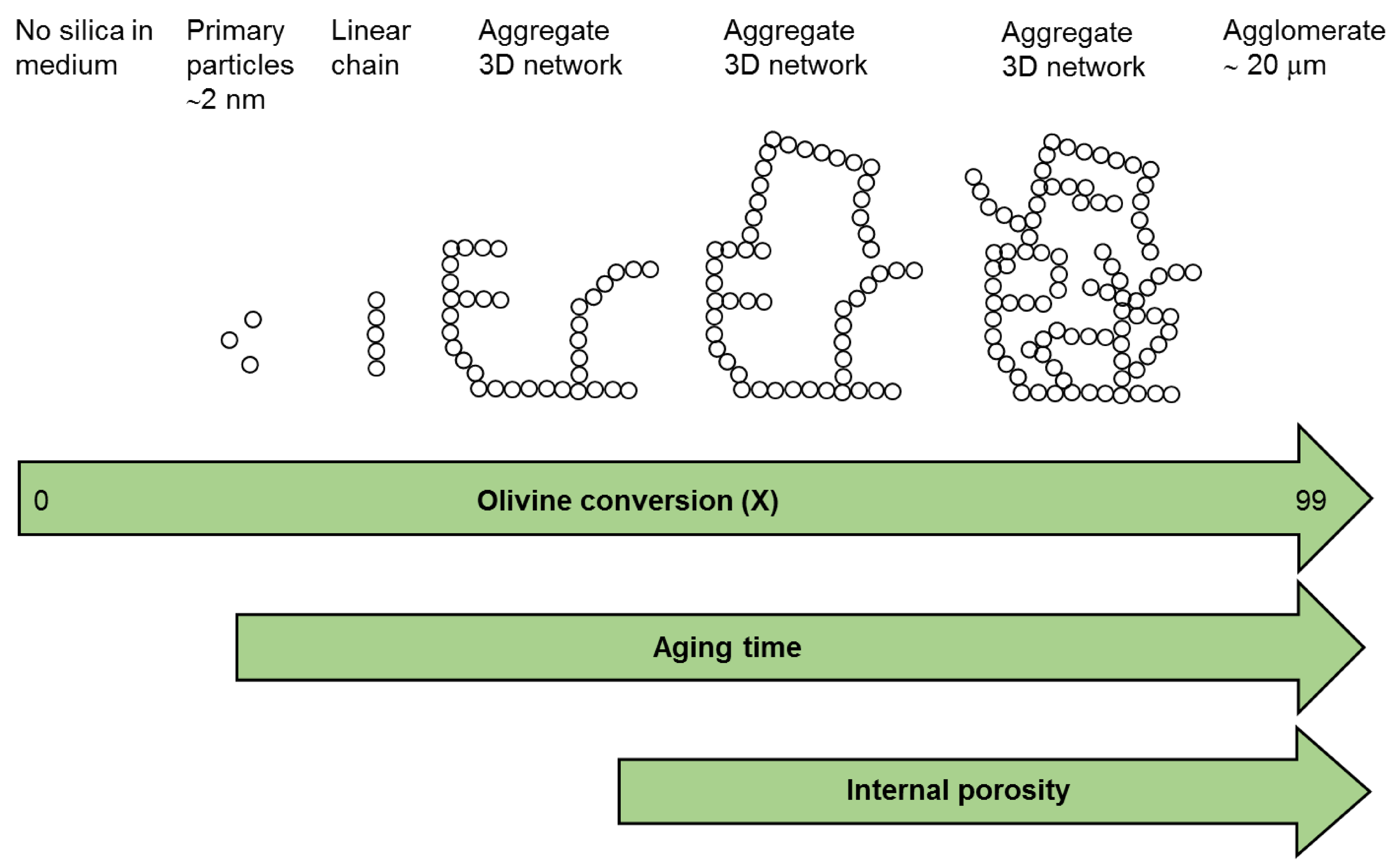


Figure 3. Texture development model of olivine nano-silica

Conclusions

1. Olivine nano-silica exhibit a SSA_{BET} in the range of 100 to 500 m^2/g.
2. The particle size of olivine nano-silica grows with time resulting in porous clusters with a size of several microns.
3. Olivine nano-silica is microporous, mesoporous and macroporous. The PoSD is in the range of 2 to 100 nm.
4. With time, the aggregates become larger and more compact, resulting in wider PoSD and lower pore volumes.

References

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