

Charge Matching of occluded Organic Structure Directing Cations in Zeolites

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Organic Structure Directing Agents (OSDAs) play a central role in synthesis of zeolites. Typically, OSDAs consist in tetraalkylammonium cations that are trapped inside of the voids of zeolites. The positive charge of the occluded cations is compensated i) by the isomorphic substitution of Si atoms by trivalent atoms resulting in negatively charged zeolite framework; ii) by the presence of framework defects consisting in the Si-O⁻ species and Si-OH (silanols) and iii) by the incorporation of fluoride anions in small zeolite cages. The charge compensation method depends on the synthesis gel composition and crystallization conditions.

The exact location of the occluded OSDA has been matter of interest because it is accepted that there is a pairing between the negative zeolite and OSDA positive charges in order to maximize coulombic interactions. Thus, the distance between the highest positive charge density of the OSDA (typically on the N atom) and the negative charge associated to presence of T(III) atoms, Fluoride anions or defects must be as short as possible. This is call the charge matching effect.

Additionally, the occluded OSDA must fit inside of the voids of the zeolite and it is accepted that Van der Waals interactions drive the crystallization of zeolite towards the particular structure that host the OSDA. Thus, the final structure of the zeolite will depend on both effects, charge compensation and host-guest interactions.

In this presentation, we will introduce a new parameter in the understanding of zeolite crystallization and is the possibility of stablishing different configurations of OSDA-zeolite for charge compensation. This may drive to different location of the active acid sites in the final zeolite, which has been found to be relevant in improving catalytic performance of microporous materials.

For illustrating this idea, we will present a new zeolite, named ITQ-66, which can be synthesized as Borosilicate and Gallosilicate but not as Aluminosilicate. Depending of the final composition, B or Ga are located at different T-sites of the zeolite structure and therefore, charge compensation occurs in a different manner.

Also, we have found that compensating fluoride anions can 'jump' from one particular crystallographic location to another during the course of crystallization or just by gentle heating of pure silica RTH samples. Again, charge compensation of the occluded OSDA cations could take place by negative charges placed at different crystallographic positions.

These findings make us to conclude that charge matching mechanism is not a biunivocal relation between positive and negative charge locations. Here, we have found that inorganic compensating defects (i.e. T(III) or interstitial F anions) may be placed at different locations in the zeolite structure in presence of the same OSDA.