VI San Luis Conference
Characterization and conditioning of zeolitic tuffs to improve their catalytic features

A .J. Vinuesa[1*], **L. Bonetto**[1], **M. S. Renzini** [1], **L. B. Pierella**[1] **and C. Saux** [1]
[1] *Centro de Investigación y Tecnología Química (CITeQ) – Facultad Regional Córdoba – Universidad Tecnológica Nacional - CONICET, Maestro Lopez esq Cruz Roja Argentina, (5016) Córdoba, Argentina*
[*] *email presenting author: arielvinuesa@gmail.com*

Zeolites are usually employed as adsorbents of organic and inorganic compounds due to their high ion-exchange capacity and shape selective structure that act as molecular sieve. These crystalline hydrated aluminosilicates of Na, K and Ca consist of a three-dimensional framework, having a negatively charge lattice. This characteristic is responsible of the ion exchange capacity of these materials[1]. Because of their unique properties, such as tridimensional micropore structure, high surface area, high chemical stability, excellent absorption capacity, high thermal and mechanical stability and controllable acidity, zeolites have been widely used as catalysts and supports on heterogeneous catalysis applications. Nevertheless, the complicated and high expensive synthesis considerably restrict the application of the synthetic zeolites on remediation reactions. In this sense, natural zeolites could overcome these difficulties since their high abundance and low extraction cost make them cheap materials[2].

In this work, zeolitic tuffs from Compañía Minera Argentina (San Juan, Argentina), from now on named NZ, were characterized by means of XRD, FTIR, TG, N_2 adsorption isotherms, ICP and BET. In order to improve these natural zeolites properties, a series of conditioning treatments were applied to the raw materials. Considering that the impurities that are present in the as received solids could affect the catalytic processes results, one of the applied treatments was the washing with deionized water all night (WZ). Also, NZ were treated with HNO_3 (NAZ) and HCl (CAZ) aqueous solutions at 90 °C during 5 h under magnetic stirring. After the acidic treatment, the solids were washed with deionized water until neutral pH and further dried in oven overnight. Finally, different thermal treatments were applied under static oxidant atmosphere.

The raw and modified zeolites were extensively characterized in order to determine the effect of the applied treatments. Surface area of these porous materials showed a noticeable increment after acidic treatments (higher than 50%). This effect could be assigned to the lixiviation of ionic species inside porous structure, since porous volume also showed an increment higher than 35%. This hypothesis was confirmed by ICP results.

Nevertheless, it should be noted that acidic and thermal treatments also affected crystallinity of the samples. By XRD it was observed a reduction of Clinoptilolite signals intensities for NAZ and CAZ. When thermal treatments were applied, CAZ sample exhibited a collapse of the zeolitic structure and just quartz signals were observed. In this sense, nitric acid treatment is better in order to improve surface area, maintaining the zeolite phase of the material.

Two temperatures were evaluated for the thermal treatment of NAZ samples, 350 and 500°C. According to XRD results, the highest temperature is not recommendable, since notorious crystallinity lost was obtained. Therefore, 350°C was adopted as calcination temperature. These materials were further tested as catalysts for different procedures, such as photocatalysis for colorant degradation and catalytic pyrolysis for polymer and biomass residues valorizations.

References

1. De Velasco-Maldonado, P.; Hernández-Montoya, V.; Montes-Morán, M. A.; Aurea-Rangel Vázquez, N.; Pérez-Cruz, M.A. "Surface modification of a natural zeolite by treatment with cold oxygen plasma: Characterization and application in water treatment", *Applied Surface Science*, Vol. 434, 1193–1199, 2018.
2. Akbari Sene, R.; Sharifnia, S.; Moradi, G.R. "On the impact evaluation of various chemical treatments of support on the photocatalytic properties and hydrogen evolution of sonochemically synthesized TiO2/Clinoptilolite", *International Journal of Hydrogen Energy*, Vol. 43, 695-707, 2018.