Ethylene removal with metals-based zeolites for preservation of climacteric fruits

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Nowadays, there is a high importance of consuming fresh fruits and vegetables (F&V) in a well-balanced diet. One main issue concerning fruit preservation is ethylene molecule, a natural plant hormone that is responsible for fruits ripening and senescence. Thus, its removal from transportation and cold storage chambers is essential for industrial companies to prevent deterioration or spoilage of F&V and extend their post-harvest life [1].

Different technologies can be used to remove/avoid ethylene action: 1-MCP inhibition, $KMnO_4$ scrubbing, thermal/photocatalytic oxidation and adsorption methods. This last one uses solid porous materials, like zeolites, and seems a promising solution, as those adsorbents are highly effective for removing ethylene, in particular when using supported metals. Indeed, the high surface area and pores volume of the supports, combined with a metal that allows interaction with ethylene via π complexation [2], make these adsorbents perfect candidates for ethylene trace removal. Due to their availability and versatility, synthetic and natural zeolites have been studied for ethylene removal. In particular, the effect of the compensating cation, as well as the nature of the metal introduced (Pd, Ag, etc.) has been the focus of several studies.

In this work, we studied Ag-based ZSM-5 zeolites for the removal of ethylene, under conditions close to the ones used in cold storage chambers. Different starting ZSM-5 materials were tested (Si/Al ratio of 15 and 40, H^+ or Na^+ as compensating cation) and different amounts of silver were also used. All these parameters were evaluated in the removal of ethylene from a mixture of C_2H_4 (50 ppm), He (10% vol.) and N_2, by the means of breakthrough curves experiments; dry and wet (80% RH) conditions were also tested. Adsorption experiments were performed at 2 ºC. An analysis of variance (ANOVA) was also performed to identify the factors and interactions that affect ethylene adsorption capacity. The ethylene adsorption results obtained (see Figure 1) show that the amount of Ag plays a major role in ethylene adsorption capacity. However, for AgZSM-5 adsorbents with Si/Al of 15, although the amount of Ag is higher (because of the higher amount of Al), C_2H_4 capacity only increases slightly, meaning that other factors (like the nature of the compensating cation and the Si/Al ratio) may also play a role as well. In Figure 2, interestingly, it is possible to see that H_2O can compete with C_2H_4 as $C/C_0 >> 1$. Nevertheless, by decreasing the amount of H^+ species (by increasing the amount of Ag and/or replacing Na^+ for H^+) competitive adsorption with water can be drastically reduced, improving the final ethylene adsorption capacity of the adsorbents.

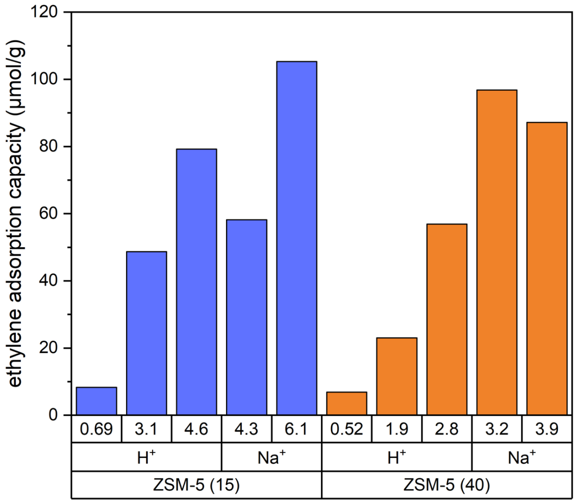

Figure 1. Ethylene capacity of AgZSM-5 zeolites with different amounts of silver (blue: Si/Al = 15; orange: Si/Al = 40) (80% RH)

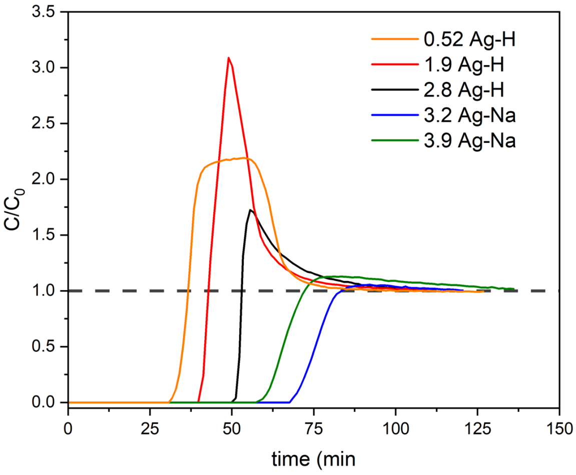

Figure 2. Breakthrough curves of AgZSM-5 zeolites (Si/Al of 40) with different amounts of Ag.

Some characterizations were performed to determine the nature of the Ag species responsible for the good performance of the various adsorbents. XRD results only show the peaks from ZSM-5 material, meaning that no peaks contribution from either Ag_2O or Ag phases could be observed. On the other hand, UV-Vis DRS results show that all the spectra are dominated by Ag^+ species. However, from H_2-TPR experiments (see Figure 3), it is possible to distinguish $Ag_n^{\delta+}$ species (250-600 ºC) from Ag^+ ones (50-250 ºC), making possible the quantification of both species. If no direct correlation can be obtained between the ethylene capacity and the total amount of Ag for each sample, a fair linear relationship (Figure 4) is observed between the amount of C_2H_4 adsorbed and the amount of Ag^+ species (from H_2-TPR), showing the importance of these species in the adsorbents performance. Some regeneration tests were also performed and showed that adsorbents were capable to maintain their C_2H_4 capacity, even after three consecutive adsorption-regeneration cycles.

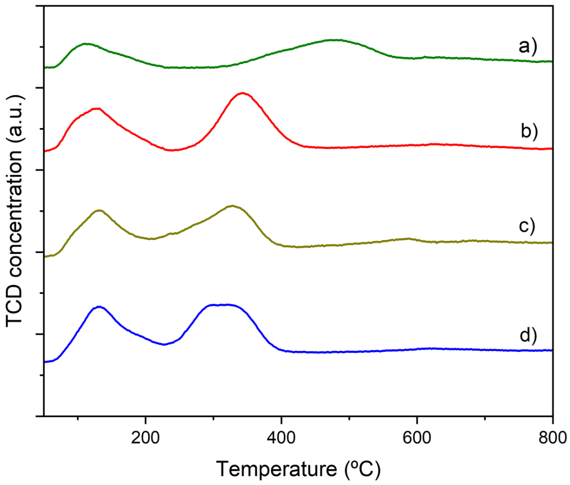

Figure 3. H_2 TPR for the Ag based zeolites with Si/Al of 40 (Ag content in wt.%: a) 1.9; b) 2.8; c) 3.2 and d) 3.9)

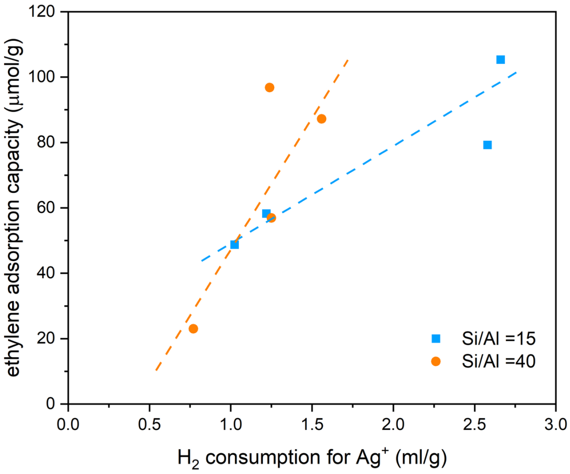

Figure 4. C_2H_4 adsorption capacity as a function of H_2 consumption from Ag^+ species for AgZSM-5 adsorbents.

The statistical analysis performed was useful for modelling and analysing the response surface where the ethylene adsorption capacity was modelled as function of tested parameters (Figure 5). By analyzing the model results, it is possible to verify that the greater the amount of Ag, the greater the ethylene adsorption capacity and that there is an interaction between Si/Al ratio and Na exchange rate that impact the results. For ZSM-5 with a lower Si/Al ratio (15) (Figure 5A), better results are obtained in terms of ethylene adsorption capacity when using the zeolite in the proton form, while for Si/Al ratio of 40 (Figure 5B), it is preferable to work with the Na form. In this last situation, it is possible to obtain the highest value of ethylene adsorption capacity in an atmosphere of 80% RH.

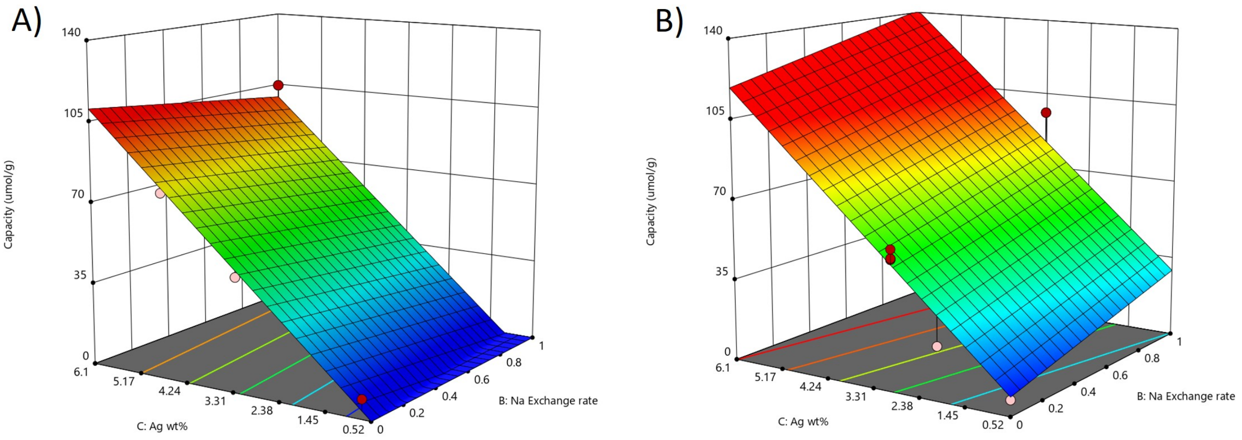

Figure 5. A three-dimensional response surface showing expected ethylene adsorption capacity (wet conditions) as a function of Ag wt% and Na exchange rate. (A) for ZSM-5 with Si/Al ratio of 15 and (B) for ZSM-5 with Si/Al ratio of 40.

References

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