Experimental report

07/09/2022

Proposal:	**7-05-522**	**Council:**	4/2020

Title: INS study of ethen on Ag+ cations exchanged on Chabazite and Faujasite zeolites

Research area: Chemistry

This proposal is a continuation of 7-05-488

Main proposer:	**Teresa BLASCO**
Experimental team:	Monica JIMENEZ RUIZ
Local contacts:	Monica JIMENEZ RUIZ

Samples:
Faujasite zeolite (Si/Al=40), Ag+
Faujasite zeolite (Si/Al=5), Ag+
Chabazite zeolite (Si/Al=40), Ag+
Chabazite zeolite (Si/Al=5), Ag+

Instrument	Requested days	Allocated days	From	To
IN1 LAG	7	5	29/01/2021	31/01/2021
			14/02/2021	17/02/2021

Abstract:

Many chemicals and polymers relies on the production of ethene that exceeded 144 million tons in 2015, mostly by steam cracking. The separation of ethene from other hydrocarbons is actually carried out by the cryogenic distillation. The high energy demand of this technology makes desirable the development of new processes, being the zeolites based separation the most promising. This alternative route takes advantage of the molecular sieving properties of zeolites and the possibility of tuning their polarity. One approach to adjust the polar character of silicoaluminate zeolites is by the presence of cations in the voids channels and cavities. Here, we propose to study the interaction of ethene adsorbed on small pore zeolite Chabazite (CHA) and a large pore zeolite Faujasite (FAU) with Si/Al ratios of 5 and 40 and having as counter-cations silver. We think that INS is the ideal spectroscopic technique for understanding the mechanism of ethene-zeolite interaction, particularly when combined with advanced Solid State NMR studies and theoretical calculations.

The production of ethylene exceeds 200 million tons per year[1], consolidating this molecule as a critical feedstock material for petrochemical industry. A fundamental step for the application of this alkene in derivatives is its separation/ purification from ethane after being obtained by naphta or ethane steam cracking. The state of art method for such task is cryogenic distillation, one of the most energy consuming industrial processes nowadays[2].

Porous solids adsorbents have been addressed as a highly promising alternative solution for this matter, being represented by Metal Organic Frameworks (MOFs) and zeolites. While some MOFs may present a rather poor stability[3], zeolites have been standing the roughness of industrial applications since the 1950's[4]. Another great advantage of zeolites is their tunability in terms of pore size, shape and surface functionality, allowing specific selective adsorption processes even at ambient temperatures. Due to the small differences of ethylene and ethane kinetic diameters (which is only 0.028nm) and their nearly identical physical properties, molecular sieving effect by itself is not effective for their separation. Thus, this process must rely also on a Lewis acid-base interaction between the alkene and a transition metal cation, specially Cu(I) and Ag(I)[5,6], allocated in the adsorbent. Nevertheless, the exact adsorption mechanism of ethylene on Ag(I) exchanged CHA, for example, is not completely understood yet.

In this work, we characterized this interaction between ethylene and silver aluminossilicate CHA at a microscopic level using a multidisciplinary approach involving Inelastic Neutron Scattering (INS), Nuclear Magnetic Resonance (NMR), UV-vis and Density Functional Theory (DFT) calculations parting from a real system. From UV-vis analysis, it was seen that the system under investigation contains not just cations but also charged Ag clusters. Both species interact with the ethylene, as confirmed by the comparison between the experimental INS spectrum and the DFT calculated INS spectra obtained for a cationic and a cluster models. ^{13}C-Solid State NMR showed an upfield shift from 123 ppm to 110 ppm, suggesting a stronger proton shielding and electron transfer between the adsorbant/adsorbent. This fact was corroborated by DFT electron density difference calculations, proving the nature of this interaction, known as π-complexation. Finally, by analysing the red shift of C-C stretching modes and C-C bond lengthening with information provided by INS and DFT, we could not just have a further confirmation of its nature, but could also evaluate the extension of the interaction for each model, attesting the higher preference of ethylene to cationic Ag species in such a complex system (Fig.1).

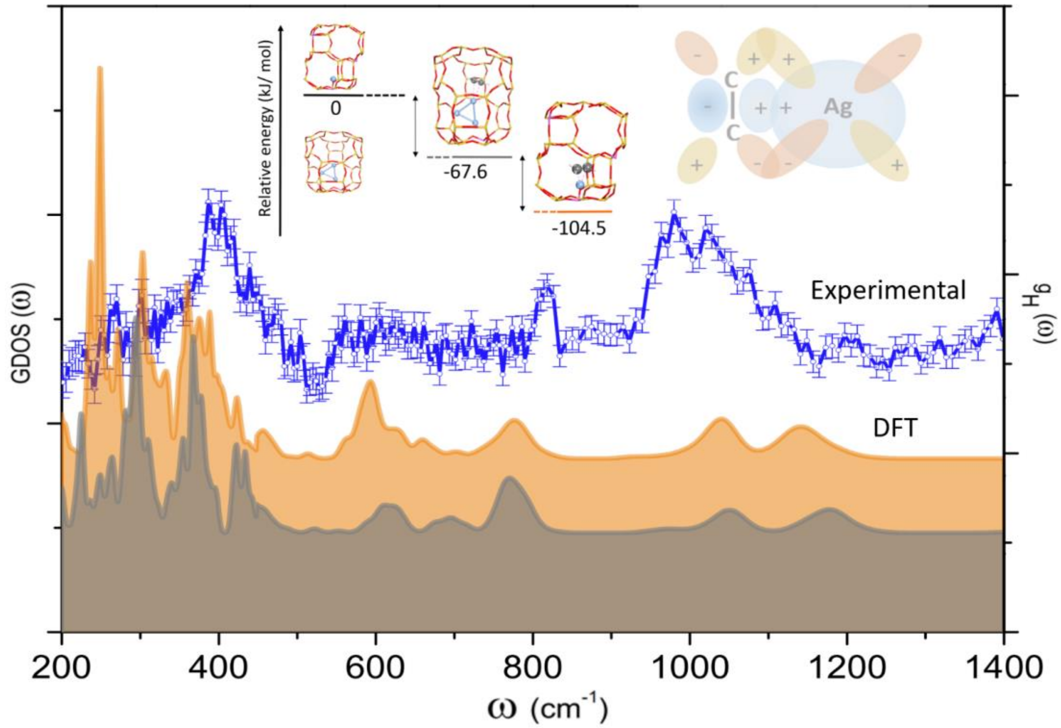

Figure 1: Experimental and calculated INS for Ag+ and Ag3+ systems, showing the preference of ethylene towards Ag+. Despite the energy difference, the behaviour of the interaction does not change drastically as suggested by similar INS spectra.

References

[1] Y. Wang, S. B. Peh, D. Zhao. Small, **15**, 1900058 (2019) [2] D. Saha, M. Kim, A. J. Robinson, R. Babarao, P. K. Thallapally. iScience, **24**, 103042 (2021) [3] M. Ding, X. Cai, H. L. Jiang. Chem. Sci., **10**, 10209 (2019) [4] J. D. Sherman. PNAS, **96**, 3471 (1999) [5] M. Sun, Q. Gu, A. Hanif, T. Wang, J. Shang. Chemical Engineering Journal, **370**, 1450 (2019) [6] Y. Chai. Science, **368**, 1002 (2020).