Experimental report

18/04/2023

Proposal: 7-05-569 **Council:** 10/2022

Title: Mobility of pi-complexes of C2H4 with Ag+ species in Ag-zeolites by Quasielastic Neutron Scattering

Research area: Chemistry

This proposal is a new proposal

Main proposer: Gabrielli maria E SILVA DE ALMEIDA

Experimental team: Alessandra DE MARCOS GALAN
Teresa BLASCO
Fernando REY
Alberto BARROS

Local contacts: Jacques OLLIVIER

Samples: AgNaCHA Si/Al = 4 Na/Al = 0.17 Ag/Al = 0.54
AgNaCsRHO Si/Al=5 Na/Al = 0.09 Cs/Al=0.33 Ag/Al=0.48
AgHLTA Si/Al = 5 Ag/Al = 0.24 H/Al=0.76

Instrument	Requested days	Allocated days	From	To
IN5	4	2	31/03/2023	04/04/2023

Abstract:

Ag-zeolites have obtained an increasing interest due to their unique capacity for ethylene/ethane purification, which is an essential process for the petrochemical industry. Very specific properties and the stability of Ag(C2H4)+ complexes within zeolites pores are highly sensitive to the dimension and geometry of such pores. Along with INS data already investigated, detailed information can be obtained by studying the molecular mobility of ethylene¿s internal rotations on an Ag+ site and even translational migration among the sites at the scale of 1 ps. Here we propose to perform the characterization of the molecular mobility of ethylene bound to Ag+ site in zeolites CHA, LTA and RHO by Quasielastic Neutron Scattering, which has never been applied in these specific systems before as far as we know.

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Ag-zeolites and C_2H_4 interaction

In the first part of this experiment, we focused on Ag-zeolites (CHA, LTA and RHO types) loaded with ethylene.

Ag – exchanged zeolites have been facing an increasing interest due to their potential applications for alkene/alkane purification, which is one major challenge in petrochemical industry [1]. The selective adsorption of ethylene on Ag/zeolites has been suggested to occur through the formation of stable π-complexes with Ag+ cations [$Ag(C2H4)^+$] located within the zeolite pores and cavities [2].

The aim of this project is to investigate, in details, motions in these π-complexes located in zeolites CHA, LTA and RHO. We also intend to analyze how this interaction changes by varying the type of cavity (zeolite framework: CHA, LTA and RHO). Quasielastic neutron scattering is a unique technique for studying both the dynamical and geometrical aspects of such molecular motions, therefore leading to a more complete overview on the adsorption process.

We measured 3 Ag-zeolites:

1. **Ag-CHA-4**: Ag+ exchanged Chabazite zeolite with a Si/Al ratio = 4.

2. **Ag-LTA-4**: Ag+ exchanged LTA zeolite with a silica ratio = 4.

3. **Ag-RHO-4**: Ag+ exchanged RHO zeolite with a Si/Al ratio = 4.

Table 1: measured samples @ IN-5 at temperature range from 50K to 235K.

SAMPLE	FILES	
	EMPTY	LOADED (1 C_2H_4/u.c.)
Ag-CHA-4	#228322-228387	#228436-228544
Ag-RHO-4	-	#228565-228597
Ag-LTA-4	-	#228599-228629
Empty cell #1	#228633-228639	-
Empty cell #2	#228646-228649	-

Each set of zeolite had 1.0 ethylene per unit cell (samples in quartz cells). We also considered the dry samples and their empty quartz cells, as listed in table 1. All samples were measured with a 4.8 A wavelength at 50K, 100K, 175K and 235K considering a 2hours/scan rate. In situ Ag-CHA and Ag-RHO measurements were planned. However, due to a mechanical problem in the sticks prepared for this experiment (gas leakage), it was not possible.

Figure 1 shows the signals obtained for the three systems at the extremes temperatures measured: 50 K (1.A) and 235K (1.B).

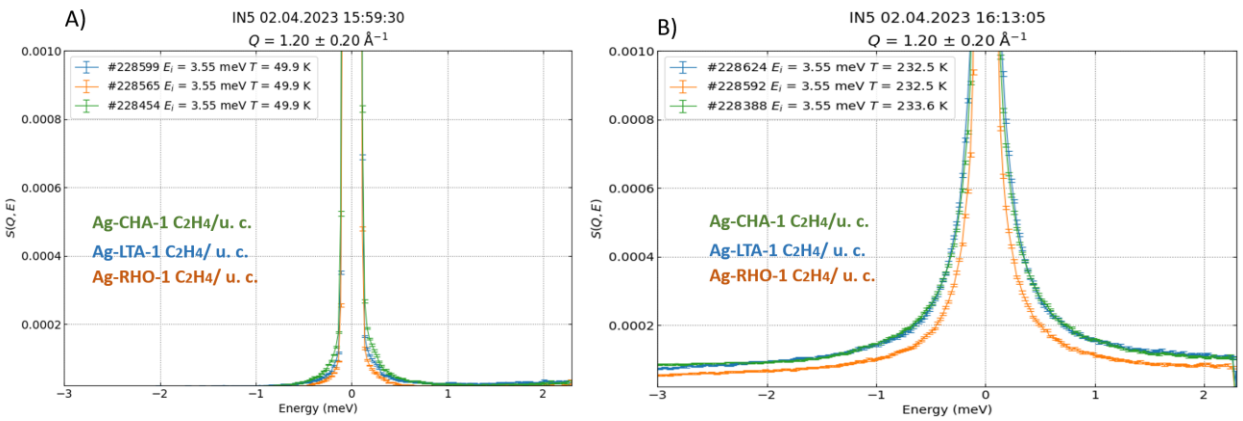

Figure 1: roughly treated QENS signals obtained for loaded samples at temperatures A) 50K and B) 235K.

For molecules in zeolites, several motions can fall within the time scale accessible on QENS instruments, such as: (a) rotational motion of the molecule on its adsorption site, (b) jumps from one preferred site to another, within the same supercage and (c) intercage diffusion [3].

From a quick interpretation, Ag-RHO system features slower and shorter motions than CHA and LTA, as expected based on previous INS data performed @IN-1 and confirmed by DFT calculations. Due to the mandatory presence of Cs^+ species in its framework, RHO cages suffers a deformation causing higher molecular hindrance. At 235K, π-complexes in LTA and CHA present a similar behavior, probably performing jumps from a 6-member ring to another inside their respective cages. The molecule avoids central positions in the cages, occupying spaces closer to the cavities walls or extremities.

As we were granted 2 more days @IN5, we performed extra experiments with the same zeolite structures using another gas: NH_3.

Ag-zeolites and NH_3 interaction

In the additional days of the experiment, we wanted to measure Ag-CHA and Ag-RHO with on ammonia molecule per silver.

NH_3-SCR is the main mechanism for the removal NOx of the exhaust gases in vehicles using urea tank as a precursor of the NH_3 as reducing agent. [4] However, the problem of this technology is the NH_3 emissions to the atmosphere. So, one alternative is the use of silver-supported catalyst on the selective catalytic oxidation of NH_3 (NH_3-SCO) reaction [5], due to its excellent catalytic behavior and the production of N_2 as main product. [6]

The main aim of this work is to determine the interaction between ammonia molecules and silver species on silver containing zeolites (CHA and RHO types), depending on the cation present that compensates the charge on the zeolite (H^+, Na^+ or Cs^+).

We measured 3 zeolites:

1. **Ag-RHO-5**: Ag+ exchanged RHO zeolite with a Si/Al ratio = 5.

2. **NaCs-RHO-5**: RHO zeolite with a silica ratio = 5.

3. **Ag-CHA-5**: Ag+ exchanged Chabazite zeolite with a Si/Al ratio = 5.

Table 2: measured samples @ IN-5 at temperature range from 50K to 235K.

SAMPLE	LOADED (1 NH_3/Ag)
Ammonia	#228663-228675 #228765-228769
Ag-RHO-5	#228676-228724
RHO-5	#228725-228760
Ag-CHA-5	#228787-228821

Ag-zeolites have loaded with one ammonia per silver, while RHO has loaded with one molecule per unit cell (samples in quartz cells). All samples were measured with a 4.8 A wavelength at 50K, 100K, 175K and 235K considering a 2hours/scan rate. We also recorded an ammonia cell at 175K, 235K and 265K. The experiments are shown in table 1.

Figure 2 shows the signals obtained for the three samples at 50 K (2A) and 235K (2B).

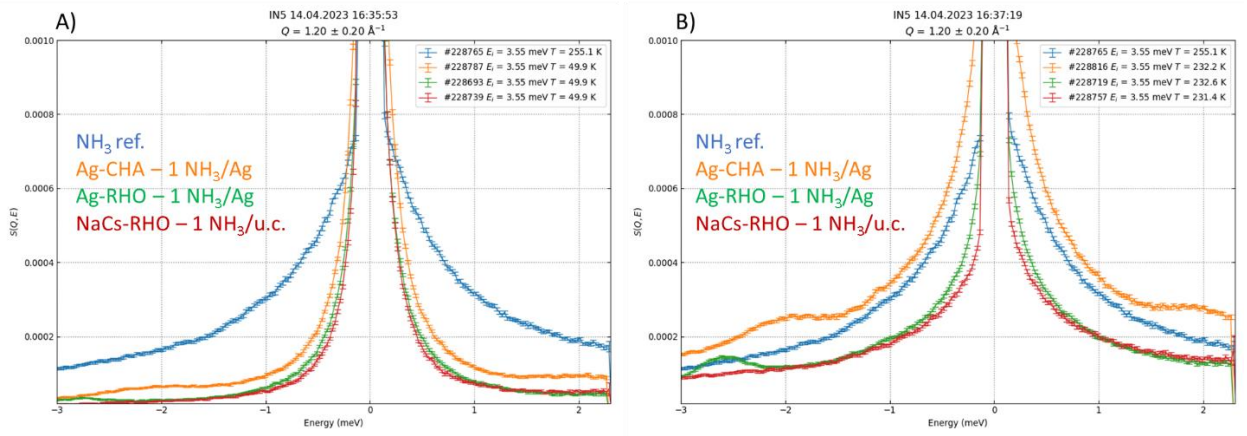

Figure 2: roughly treated QENS signals obtained for loaded samples at temperatures A) 50K and B) 235K.

As in the case of ethylene, RHO system presents slower and shorter motion than CHA system, regardless of the presence of silver cation, as expected based on previous results. At high temperature, Ag-CHA system seems to have higher motion than ammonia. This phenomenon could be due to the amount of ammonium in the ampoule, and as the temperature increases, the vibration of the molecules prevents their free movement. However, it will be necessary to wait for a more detailed analysis of the data.

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] H. Jobic. *Microporous and Mesoporous Materials.* 55, 159–169 (2002) [4] M. Moreno-González, A. E. Palomares, M. Chiesa, M. Boronat, E. Giamello, T. Blasco. *ACS Catalysis*, 7, 3501-3509 (2017) [5] L. Chmielarz, M. Jabłońska *RSC Advances*, 5, 43408-43431 (2015)[6] F. Wang, G. He, B. Zhang, M. Chen, C. Zhang, H. He, *ACS Catalyst*, 9, 1437-1445 (2019).