



# Dynamics of guest molecules in pillared zeolites studied by NMR



Saint-Petersburg State University, St. Petersburg, Russia

Centro de Nanociencias y Nanotecnología, UNAM, Ensenada, Mexico

M.G. Shelyapina

R. Yocupicio-Gaxiola

D. Nefedov

V. Petranovskii

ASCO-NANOMAT 2022  
Sixth Asian School-Conference on Physics and Technology of Nanostructured Materials  
April 25 - 29, 2022 – Vladivostok – Russia

S. Fuentes

Layered zeolites are used as precursor for mesoporous catalysts. For the successful development of these materials, knowledge on the surface structure, dynamics of guest molecules and host-guest interaction are highly required. Recent work has demonstrated that water can positively influence reaction rates in zeolite-catalyzed chemistries. Due to water molecules have high polarity and ability to form an extensive hydrogen-bonding network among themselves, bulk water, in the both liquid and solid state, exhibits very high internal cohesiveness. In restricted geometries the water molecules can also interact with the surfaces. Due to a competition between the surface-water and water-water interactions new structures of water may appear. Mesoporous silica or zeolites provide spectacular examples of the impact of nanoconfinement on the water structure and behavior. Both water structure and dynamics can be probed by proton nuclear magnetic resonance [1]. In this contribution we report on the results of our  $^1\text{H}$  NMR study of the dynamics of water molecules confined in interlamellar space of pillared mordenite and ZSM-5 zeolites.

## PREPARATION METHODS AND EXPERIMENTAL

Zeolites MOR and ZTS-5 (MFI) were synthesized hydrothermally in an one-pot method as follows [2]: In the synthesis of zeolite MFI, 3.123 g of CTAB, 0.5205 g of PEG 20000, 2.66 g of TPABr, and 0.47 g of NaOH were completely dissolved in 36.3 mL of  $\text{H}_2\text{O}$ . Then 21.46 g of sodium silicate solution (25 wt. % of  $\text{SiO}_2$  and 10.6 wt. % of  $\text{Na}_2\text{O}$ ) was added, and the mixture was vigorously stirred for 20 minutes. A solution of sodium aluminate prepared by dissolving 0.48 g of  $\text{NaAlO}_2$  in 26.6 g of  $\text{H}_2\text{O}$  was then added dropwise. Finally, 26 g of a 10 wt %  $\text{H}_2\text{SO}_4$  solution was added under vigorous stirring. For zeolite MOR, 3.123 g of CTAB, 0.5205 g of PEG 20000, and 1 g of NaOH was completely dissolved in 36.3 mL of  $\text{H}_2\text{O}$ . Then 21.46 g of sodium silicate

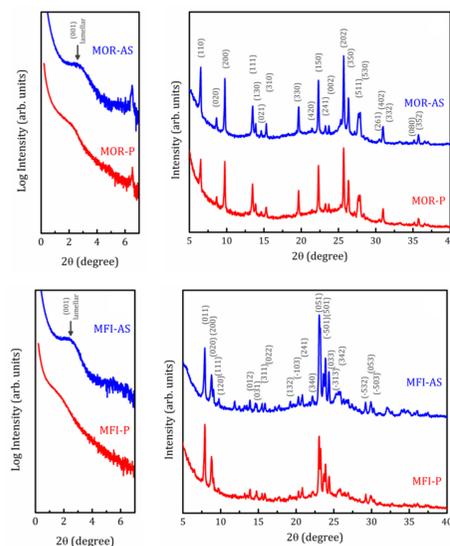
solution (25 wt. % of  $\text{SiO}_2$  and 10.6 wt. % of  $\text{Na}_2\text{O}$ ) was added and the mixture was vigorously stirred for 20 minutes. A solution of sodium aluminate prepared by dissolving 0.48 g of  $\text{NaAlO}_2$  in 26.6 g of  $\text{H}_2\text{O}$  was then added dropwise. Finally, 26 g of a 10 wt %  $\text{H}_2\text{SO}_4$  solution was added under vigorous stirring.

**Crystallization:** The mixtures were heated at 150  $^\circ\text{C}$  for 4 days in a stainless steel autoclave with Teflon coating under autogenous pressure. After that, all samples were filtered and washed with distilled water, then washed with methanol under refluxing for 12 hours at 60  $^\circ\text{C}$  to remove physically occluded surfactants. Finally, they were calcined at 550  $^\circ\text{C}$  for 4 hours.

## XRD STUDIES

Powder XRD analysis was done on a Bruker D8 DISCOVER diffractometer using monochromatic  $\text{CuK}\alpha$  radiation. SAXS patterns were recorded in a scan range from 0.2 to 7.0  $2\theta$  degree.

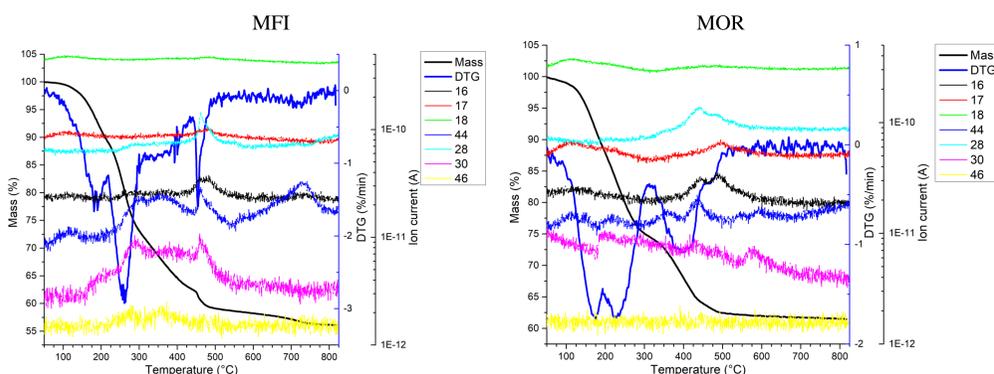
For the both samples the XPD patterns exhibit typical features of the corresponding zeolite structure with an amorphous halo (range  $2\theta$  between 17-30 degrees). Small angle X-ray scattering (SAXS) patterns unambiguously indicate the formation of lamellar mesophases. For lamellar samples, the peak at  $2\theta = 2.7^\circ$  for MOR-AS and  $2\theta = 2.3^\circ$  for MFI-AS, corresponds to the (001) reflections with interplanar distances  $d = 3.2$  and 3.8 nm, respectively. The pillaring results to increasing the interplanar distance ( $d = 4.0$  and 5.2 nm for MOR-P and MFI-P, respectively).



## THERMAL ANALYSIS OF AS PREPARED SAMPLES

Netzsch STA 449 F1 Jupiter coupled with a quadrupole mass spectrometer QMS 403 Aëolos.

The temperature range 40-900 $^\circ\text{C}$  at the heating rate of 10 $^\circ\text{C}/\text{min}$  in argon stream at the rate of 90 ml/min.



Below 220  $^\circ\text{C}$ : water release  
Above 220  $^\circ\text{C}$ : decomposition of organic molecules CTAB and TPABr.

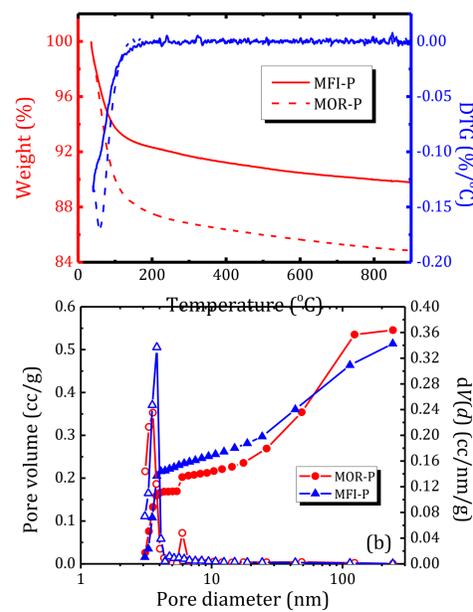
Below 300  $^\circ\text{C}$ : water release  
Above 300  $^\circ\text{C}$ : decomposition of organic molecules (CTAB).



## ACKNOWLEDGEMENTS

The samples were synthesized at CNyN-UNAM and studied at the Research Park of Saint Petersburg State University (Thermogravimetric and Calorimetric Research Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics).

## THERMAL & TEXTURAL ANALYSIS OF THE PILLARED SAMPLES



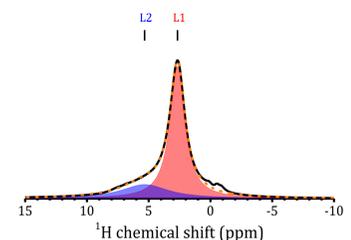
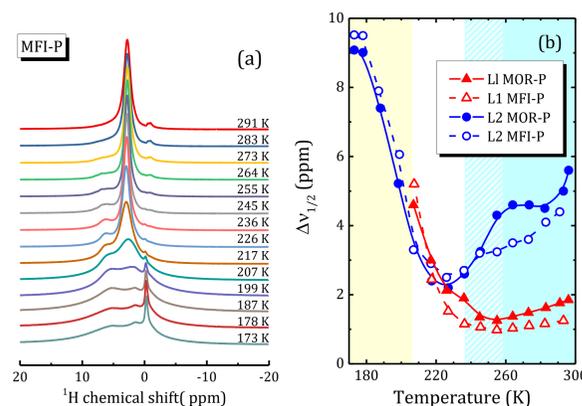
MOR-P demonstrates a higher water content compared to MFI-P (14.3 and 10.1 wt. %, respectively). For both samples, the peak of water release corresponds to about 55  $^\circ\text{C}$ , can be associated with the release of water from mesopores. For a sample of pillared mordenite, there is also a small peak (less than 8% of the total intensity) at 102  $^\circ\text{C}$ , which may be associated with the release of water from micropores.

$\text{N}_2$  physisorption isotherms were recorded at 77 K using a QuadraSorb SI instrument. Both micropores and mesopores are present. For MOR-P, the main contribution to mesoporosity is made by pores with a diameter of 4 nm, but there are also pores with a diameter of 7 nm. The total pore volume is 0.546 cc/g. The MFI-P sample is characterized by a monomodal mesopore size distribution with a pore diameter of about 3.9 nm. The total pore volume is 0.514 cc/g.

## $^1\text{H}$ NMR STUDY (SPECTROSCOPY AND RELAXATION)

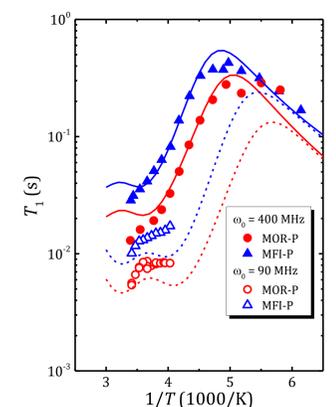
$^1\text{H}$  NMR experiments were done using a Bruker Avance IIIITM 400 MHz solid-state NMR spectrometer. In MAS experiment the rotation frequency was equal to 12 kHz. Spin-lattice relaxation times ( $T_1$ ) were measured by inversion-recovery method at 400 and 90 (Bruker SXP 4-100 spectrometer) MHz.

$^1\text{H}$  NMR studies (rotation at a magic angle and NMR relaxation) were performed. Studies have shown that for both samples, the  $^1\text{H}$  NMR spectrum at room temperature consists of two lines: 2.7 ppm intense and 5.2 ppm less intense, which can be attributed to water protons interacting with the surface of the pillared zeolite and bulk water in mesopores, respectively.



Analyzing the temperature dependence of the spectral parameters of the lines, it is possible to identify various modes of water behavior in the nanoconfinement, as well as to determine the freezing temperature of bulk water (about 180 K) and, using the Waugh-Fedin ratio, the activation energy associated with this process (about 28 kJ/mol).

The temperature dependence of  $^1\text{H}$   $T_1$  also indicates the complex dynamics of water molecules in the mesopores of pillared zeolites: there are at least three different processes with different activation energies. The use of the exchange relaxation model [3] made it possible to separate different types of proton motion and determine the corresponding activation energy and pre-exponential factor in the Arrhenius equation. In particular, for a sample of pillared mordenite, three different processes can be distinguished with activation energies of 24.5 kJ/mol (movement of a water proton interacting with the zeolite surface), 8.5 kJ/mol (rapid rotation of water protons not bound by hydrogen bonds) and 31.0 kJ/mol (freezing of bulk water). The latter is in good agreement with the  $^1\text{H}$  NMR spectroscopy measurement. For MFI-P, there are also three processes with motion parameters similar in pillared mordenite.



## CONCLUSION

A complimentary  $^1\text{H}$  NMR spectroscopy and relaxation study reveals a complex behavior of nanoconfined water in zeolite with hierarchical porosity: MOR-P and MFI-P. Distinct activation energies can be attributed to different types of water motion. The obtained results will be helpful to understand behavior of other adsorbed molecules in presence of water.

## REFERENCES

- V.I. Chizhik, Y.S. Chernyshev, A.V. Donets, V.V. Frolov, A.V. Komolkin, M.G. Shelyapina, Magnetic resonance and its applications, Springer International Publishing, Heidelberg, New York, Dordrecht, London, 2014.
- M.G. Shelyapina R.I. Yocupicio-Gaxiola I.V. Zhelezniak, M.V. Chislov, J. Antúnez-García, F.N. Murrieta-Rico, D. Homero Galván, V. Petranovskii. S. Fuentes-Moyado, Molecules **25** (2020) 4678.
- V.I. Chizhik, V.S. Kasperovich, M.G. Shelyapina, Y.S. Chernyshev. Int. J. Hydrogen Energy. **36** (2011) 1601