In operando alcohols reactivity on nanoconfined zeolitic systems

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Summary and Objectives

Dehydration of alcohols is an important industrial process, currently performed on an industrial scale using LTA-type zeolite catalysts [1,2], that would seem to provide an interesting alternative to perform organic chemistry reactions based on renewable sources, thereby reducing the energetic costs and the associated large amounts of CO_2-greenhouse gas emissions.

As an example, ethylene is a commodity product that is used daily by millions of people (from plastic water bottles to adhesives), with a global demand above 156 million tons annually [3]. Currently, the ethylene is mainly produced from fossil fuels, but the interest of ethylene production from ethanol (or bioethanol) has been growing as an environmental alternative to fossil fuels. However, ethanol dehydration is a zero-order endothermic reaction that favors the production of ethanol, thus high temperatures and pressures are needed to drive the equilibrium in favor of the production of ethylene [4], and the choice of a catalyst with high selectivity for ethylene production in these conditions is a challenge. Among different materials, zeolites are being widely used in this application since they possess the advantages of a high degree of dehydration, low energy consumption, permanence of the bed and the absence of harmful emissions to the environment.

For this reason, understanding the behavior of water and alcohols in zeolite membranes is of key importance at industrial scale, to design and optimize these types of membrane separation processes. Hence, the main goal of this proposal was to provide experimental spectroscopic evidences on the vapour/solid interactions phenomenon occurring at the nanometric scale inside the zeolite nanocages of varied topology (e.g., LTA, MFI) using alcohols of different composition (i.e., methanol and ethanol) near ambient temperature.

State of the art and background

Dehydration of alcohols is an important industrial process, currently performed on an industrial scale using LTA-type zeolite catalysts [1,2], that would seem to provide an interesting alternative to perform organic chemistry reactions based on renewable sources, thereby reducing the energetic costs and the associated large amounts of CO2-greenhouse gas emissions.

The ethanol to olefins process using bioethanol (e.g. ethanol produced from biomass gasification) is an alternative is to produce ethylene (ethylene is the main primary intermediate in petrochemistry, used for the production of ethylene oxide, ethylene dichloride, linear low density and high density polyethylene, etc.) from catalytic dehydration of bioethanol following the reaction:

C2H5OH→C2H4+H2O H298=+44.9kJ/mol

This endothermic reaction is thermodynamically favored at temperatures above 200-300`C, thus it has been applied at industrial level since 60s using alumina and zeolites as catalysts. Currently, ethylene is produced commercially by hydrocarbon cracking or by separation of refinery gas (byproduct of fluid catalytic cracking of heavy oils) [5].

On the other hand, methanol is a key ingredient in the synthesis of many organic molecules (world production was above 94 MTA in 2016), as well as a chemical feedstock or as a transportation fuel. It can also be converted to ethylene and propene, two of the largest volume petrochemical feed stocks. Furthermore, the conversion of methanol to olefins (MTO) over adequate catalysts allows to obtain petrochemical and gasoline based products from raw materials other than conventional oil based substances. When zeolites as used as catalyst for the MTO reaction C2 to C4 olefins are the dominant products, while light olefins are more difficult to obtain selectively [6]. Another challenge is that zeolites may suffer from rapid deactivation due to the deposition of carbonaceous residues in the pores that block the reactants from accessing the active sites [7].

Since the acidic/basic nature of the zeolite has as strong effect on the conversion, selectivity, and deactivation, the aim of this study is to investigate the adsorption of ethanol and methanol (alcohols with different alkyl chain length) on zeolites showing different Bronsted and Lewis acid sites (i.e., zeolites with different topology, number and type of cations to compensate the charge of the framework).

Results

Zeolites Selection

The zeolites used for this study were pure silica MFI and the aluminosilicate NaY (Faujasite topology) with 54 sodium extraframework cations. Na-Y was purchased from Zeolyst International (CBV100), and pure silica MFI was kindly supplied by ITQ (CSIC, Spain).

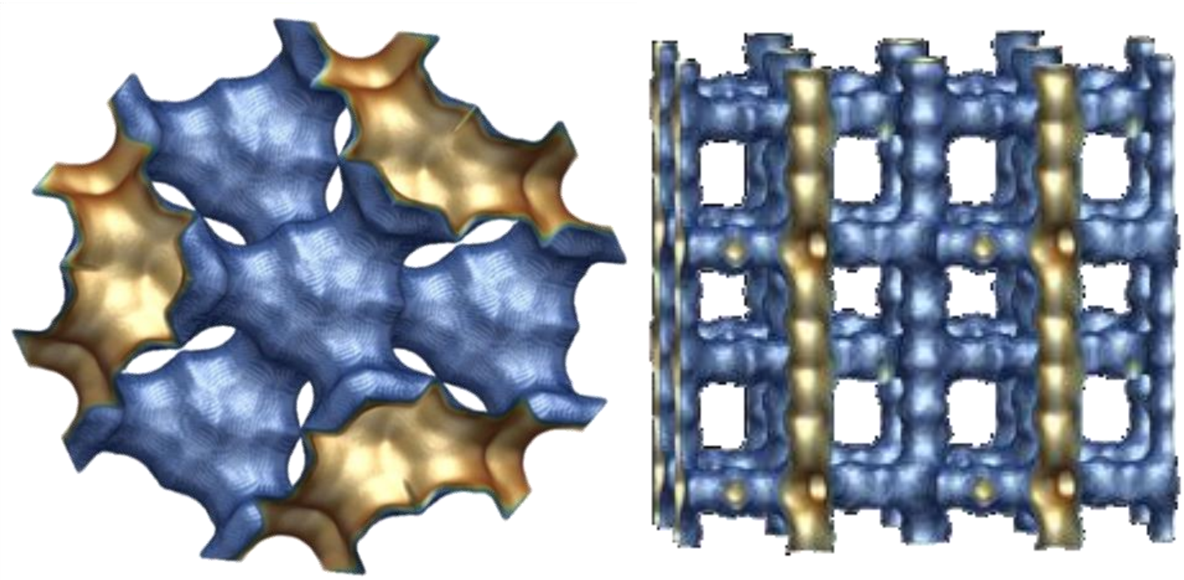

Figure 1. Grid energy landscapes of the studied zeolites: Na-Y (left) and pure silica MFI (right) [8,9].

MFI-type zeolite has a unique structure characterized by two sets of interconnecting channels defined by ten-membered (Al,Si)O_4 tetrahedra rings, with straight channels extending in the <010> direction and sinusoidal channels in the <l00> direction. The window openings of the 10-membered rings have a diameter of 5-6 A°, enabling compounds of comparable size to enter and diffuse into the channels. The chemical composition of MFI materials is varied with frameworks showing different Si/Al ratio and thus various extra-framework cations contents (cations and water molecules). As a result, different degrees of hydrophobicity of MFI can be obtained, varying from about seven in the natural zeolite (hydrophilic phase) to infinite in pure-silica silicalite (highly hydrophobic). In silicalite, the zeolite pores are nearly empty, due to the lack of heteroatom substitutions in the framework, and only H2O molecules are usually present.

NaY has a faujasite (FAU) topology; FAU-type zeolite consists of a single unit cell of $Na_xAl_xSi1_{92-x}O_{384}$, where 96 < x < 0, with two types of oxygen atoms in the framework: oxygen atoms bridging two silicon atoms and oxygen atoms bridging one silicon and one aluminium atom. Since the cation interaction is stronger with the latter than with the former, the aluminium positions determine the cation distribution in FAU. This zeolite has a cubic unit cell dimension of 25.028 Å. FAU-type zeolites are labeled either X or Y, depending on their framework aluminium density. In this study we have used zeolite Y, which has a framework aluminium density of 54 aluminium atoms and sodium cations per unit cell, and it is formed by sodalites connected to each other.

Zeolites pre-conditioning

Due to the highly porous nature of the zeolites and their well-known affinity towards water, the zeolites were dried and stored in an oven at 100°C before their use. After mounting the samples in the capillary (sealing with beeswax), they were outgassed under high vacuum (turbomolecular drug pump) at 50°C for ca. 6-8 hours (in any case assuring a vacuum of at least 10^{-5} mbar) to clean the pore voids of the zeolites before the loading of the alcohols.

Vapor Dosing at controlled pressure and temperature conditions

The dosing of the alcohols vapors inside the zeolite was carried out in an in-house cell available at the Spanish CRG that allows the recording of XRD patterns under controlled conditions of pressure (from high vacuum to ca. 6 bar) and temperature (between 80-1000 K). Further description of the cell can be found in reference 10.

The alcoholic vapor is heated up to its boiling point in a closed vessel immersed in a water bath at controlled temperature. To avoid condensation of the vapors in the gas lines leading to the cell and the capillary, the tubes were heated at about 100°C with wrapping heating cords. During the adsorption step, it is important to control the temperature of the alcohol reservoir to keep the partial pressure of the alcohol below 2 bar (maximum pressure of the glass vessel).

HXRD measurements

HXRD patterns of the pristine (unloaded) and gas-loaded zeolites where recorded in the Branch A of the Spanish CRG BM25-SpLine beamline at the ESRF, located on the soft edge of the D25 bending magnet with a critical energy of 9.7 keV. The home-designed θ-2 θ diffractometer is equipped with a NaI(Tl) point scintillation detector in Debye–Scherrer geometry. The X-ray beam wavelength was 0.77412 A° and the beam spot size was ca. 4 x 1 mm, to ensure homogeneous conditions of temperature in the beam path across the sample mounted in a capillary. Standard Reference Material (SRM) 640c Si powder from the National Institute of Standards and Technology (NIST) was used for calibrating the wavelength and temperature and to align the diffractometer. The powder Si reference was mounted in a 0.5 mm quartz capillary. Temperature calibration was performed by fitting the thermal expansion/contraction of eight diffraction peaks of the Si reference with the thermal expansion coefficient.

The diffractometer was used in transmission configuration with quartz capillaries of 1 mm diameter and 0.05 mm thickness. Diffraction patterns were acquired at 298 K and collected in the 2θ range from 2° to 63° corresponding to a resolution of better than 0.7 A° The diffraction patterns were acquired with an angular step of 0.01° and an integration time 3 s.

Discussion

Figure 2 shows the corresponding spectra of the MFI zeolite after exposure to methanol vapours at temperature near ambient conditions and exposure to argon at cryogenic temperature (e.g., 87 K). The choice of argon at 87 K was based on the fact that it is an inert gas, and the temperature allowed to reach an absolute pressure of the gas confined in the pores of the zeolite of up to 900 mm Hg. In contrast for methanol, at the experimental conditions used, the partial pressure of the vapour inside the pores of the zeolite is limited to values below 500 mm Hg.

The pattern of the sample exposed to methanol vapours was fitted to the monoclinic structure of the zeolite, which has been reported as the most stable configuration of this material at ambient temperature [8,9,11]. The structure under vacuum showed a similar pattern.

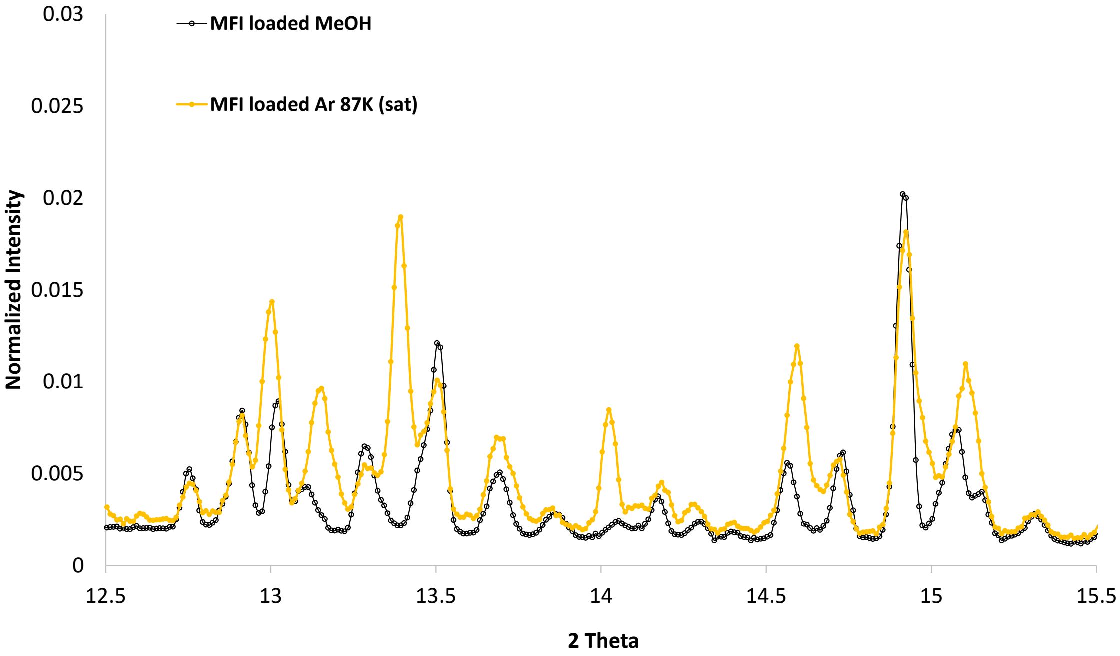

Figure 2. Example of high Resolution synchrotron X-ray diffraction patterns of pure silica MFI zeolite exposed to argon saturation (ca. 900 mmHg) and to pure methanol vapours at 298 K (ca. 500 mmHg).

As seen, the presence of argon confined in the pores provoked importance changes in the patters; some peaks associated to the monoclinic structure are visible, while some others indicate the presence of the orthorrombic one. This is surprising since the temperature of the argon loading was 87 K, far below the stability temperature for the orthorrombic configuration. Indeed, according to literature, MFI shows a reversible bi-stable behavior controlled by an external stimulus (e.g. temperature or adsorption of ammonia and other organic vapors), adopting a monoclinic configuration at temperatures below 300 K, while above this temperature the symmetry changes to orthorhombic [12]. Furthermore, the process was complete reversible, with the zeolite recovering the pattern of the monoclinic structure after desorbing the gas loaded.

All this suggests that, even if specific interactions between the zeolite and the OH moiety of the alcohol are expected during the confinement of methanol, this is not a driving force for inducing structural changes (as those observed in the case of Ar at much lower temperature). Data would suggest that this structure modification is related to the pressure of the adsorbed species confined in the pores of the zeolite rather than to the nature of the adsorbed guest itself.

The diffractograms of zeolite FAU after exposure to both Ar at 87 K and methanol at ambient conditions were also explored (Figure 3), aiming at studying the impact of the cations present on the framework.

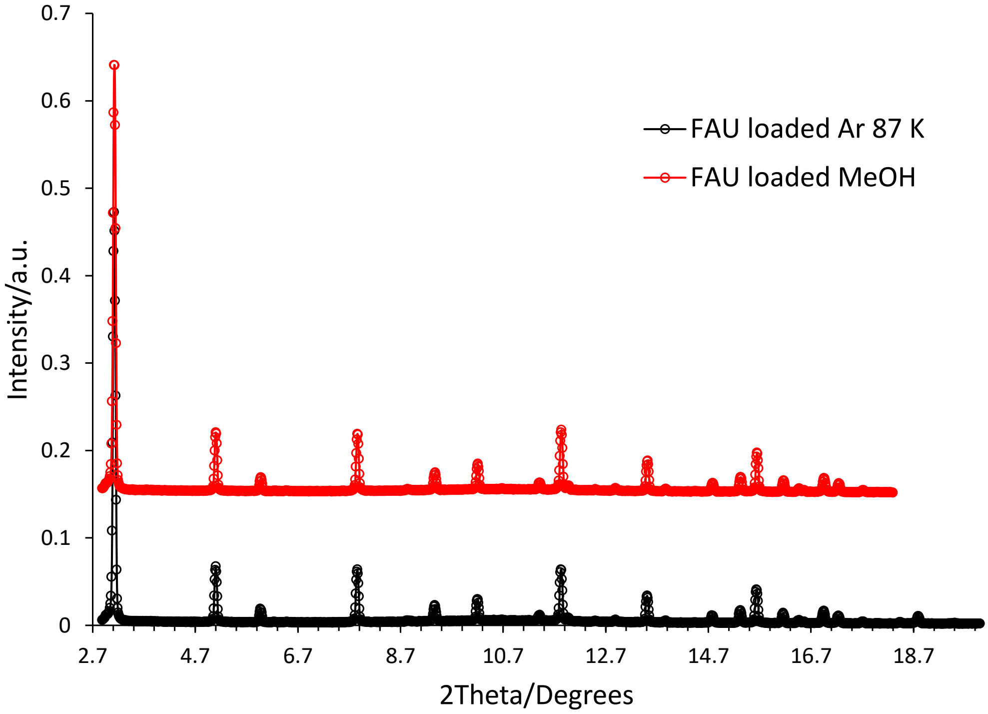

Figure 3. Example of high Resolution synchrotron X-ray diffraction patterns of sodium FAU zeolite at various conditions: under vacuum; 87 K and saturation of Ar (ca. 900 mmHg) and exposure to pure methanol vapours at 298 K (ca. 500 mmHg).

The pattern of the sample after vacuum was fitted to the cubic structure widely reported in the literature for this solid. More importantly, neither the confinement of argon nor methanol caused any structural modification on the zeolite, with similar XRD patterns for the zeolite under vacuum and loaded with these probes. Thus the presence of cations inside the framework does not seem to be important to induce structural changes

Further analysis of the obtained data, including Rietveld refinement are ongoing to evaluate and ideally quantify the extent of this phase transition, and link it with the nature of the adsorbed gas and the pressure of the adsorbed probe inside the nanopores of the zeolite.

SCIENTIFIC IMPACT OF THE RESULTS OBTAINED IN THIS PROPOSAL

We have explored the alcohol-zeolite interactions in all silica MFI and faujasite zeolites equilibrium conditions and room temperature using real time monitoring of the synchrotron HRPD patterns upon adsorption.

In this regard, in-situ evidences of structure deformation were obtained upon the adsorption of inert gases at low temperature while the exposure to methanol preserved the structure of the zeolite. This indicates that the studied seolites can be safely use for the dehydration of methanol, provided that the partial pressure inside the nanopores is controlled. The outcome of this work is expected to be published in the forthcoming year; we also expect to present several contributions to international conferences on the fields of adsorption of nanoporous materials (i.e., IberoAmerican Adsorption symposium IBA-3 and Iberian Adsorption Meeting RIA-41, to be held in Gijon 2018).

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