

**ASSESSMENT OF MASS TRANSPORT  
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NETWORKS BY COMBINING GRAVIMETRIC AND  
INFRARED SPECTROSCOPY**

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# ASSESSMENT OF MASS TRANSPORT PROPERTIES IN BIMODAL MICROPOROUS NETWORKS BY COMBINING GRAVIMETRIC AND INFRARED SPECTROSCOPY

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## ABSTRACT

Interest of this study is to develop classical macroscopic diffusion measurements to probe and allow distinguishing a true hierarchical material from the other material. To this aim, the AGIR methodology (Analysis by Gravimetry and IR spectroscopy) will be used. Gravimetric measurements provide more classical approach to molecular uptake measurements, whereas infrared (IR) spectroscopy can provide additional data on the interaction, orientation and environment of the molecules on the solid surfaces. In this study we evaluated the mass transport properties in a mechanical mixture of hierarchical H-MFI and H-FAU zeolites. Using AGIR technique, we have been able to distinguish the diffusivity of each component present in the mechanical mixture of following pure zeolites: H-MFI and H-FAU respectively. The potential and limitations of this new methodology will be discussed.

Keywords: Hierarchical zeolites; Diffusivity; AGIR.

## INTRODUCTION

Zeolites are crystalline microporous materials, are widely used because of their high surface area, strong and tunable acidity, high adsorption capacity, and hydrothermal stability. A large part of their exceptional catalytic performance is due to pore confinement effects [1,2]. Further advancement in catalysis by zeolites can be achieved by improving the limited rate of intracrystalline mass transfer that affects efficiency of each process utilizing zeolites. Addition of mesopores to their structure or use of bimodal micro-porosity can create hierarchical architecture of porosity and is a viable way to overcome these issues. While the general field of mass transport in hierarchical materials is very lively, reports on diffusion characteristics that directly assess the improved transport in the bimodal meso-micro or micro-micro porous networks are still scarce. In this work we aimed at developing a general method allowing discriminating the diffusion in each part of such a bimodal network.

To this aim, we have investigated the mass transport of isooctane in a model mechanical mixture of H-MFI and H-FAU zeolites. Such mixtures are used, for instance, in catalytic cracking (FCC) whereby the largest porous network (H-FAU) allows cracking of the largest alkanes and the smallest (H-MFI) further cracks light hydrocarbons to enhance light olefin yields. The uptake of the probe was followed using a setup combining a microbalance connected to an infrared cell, developed in our laboratory (AGIR, the french acronym for Gravimetric Analysis and IR spectroscopy) [3].

## EXPERIMENTAL

AGIR was used to measure the uptakes of isooctane in pellets of the pure zeolites and mechanical mixtures. This technique allows measuring simultaneously the pellet weight and IR spectra of the solid sample and adsorbed species under gas flow, between room temperature and 773 K [3]. Analyses were carried out on self-supported discs (diameter: 1.6 cm, 20 mg). Infrared spectra of the sample were recorded with a Nicolet 6700 spectrometer equipped with a MCT detector (16 scans/4 cm<sup>-1</sup> resolution) within a broad spectral range

(4000–400  $\text{cm}^{-1}$ ). Prior to the analysis the samples were pretreated *in-situ* under the flow of argon at 723 K for 6 h; this temperature was reached using a heating rate of 1 K  $\text{min}^{-1}$ . The uptake of isooctane with a partial pressure of 1.2 kPa in flowing Ar (total flow rate of 25  $\text{cm}^3$  (Normal Temperature and Pressure (NTP))  $\text{min}^{-1}$  and a total pressure of 101 kPa) was subsequently measured at 423 K.

In typical procedure, commercial H-MFI and H-FAU zeolites and mechanical mixtures containing 82.5 % and 17.5% of H-MFI and H-FAU, respectively, were used to study adsorption and diffusion.

## RESULTS AND DISCUSSION

Fig. 1A shows the normalized uptakes of isooctane measured at 423 K in pure H-MFI, H-FAU and the mechanical mixture of both as a function of time as determined by gravimetric analysis. As expected, the uptake of isooctane adsorbed in H-MFI is growing slowly up, while the uptake in H-FAU zeolite grows much faster because of large cavities inside H-FAU zeolite. The equilibrium uptakes obtained in the mechanical mixture were consistent with those obtained for pure zeolites. In particular, uptake of the mechanical mixture was the weighted average of the uptake of pure zeolites. Finally, Figure 1A shows a logical order of the adsorption profiles, with the following ranking: H-FAU > mechanical mixture > H-MFI.

Fig. 1B shows the normalized uptake at short times versus the square root of time for H-MFI, H-FAU and the mechanical mixture. The initial slope of these curves allows assessing the characteristic diffusion time constant  $\tau^{-1} = D_{\text{eff}}/L^2$  [4]. As expected, the diffusivity in H-FAU zeolite ( $D_{\text{eff}}/L^2 = 143 \cdot 10^{-4} \text{ s}^{-1}$ ) was much larger than in H-MFI zeolite ( $D_{\text{eff}}/L^2 = 22.9 \cdot 10^{-4} \text{ s}^{-1}$ ). For the mechanical mixture, the initial slope used to estimate the diffusivity in the mechanical mixture was  $D_{\text{eff}}/L^2 = 153 \cdot 10^{-4} \text{ s}^{-1}$ , which is close to that measured on pure H-FAU and much larger than H-MFI sample. This is because at short times, the largest part of the adsorbate diffuses in the largest porous network (H-FAU). Hence, the classical assessment of diffusion properties using gravimetric analysis does not allow distinguishing the diffusion of isooctane in each zeolite porous network.

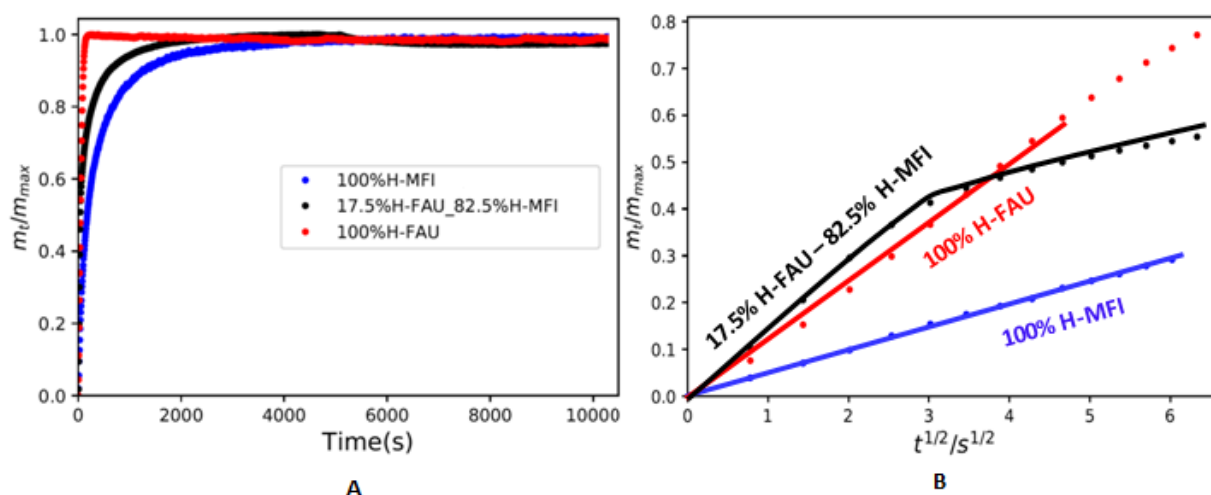


Figure 1 A: Isooctane uptake curves of the H-MFI (blue), H-FAU (red) zeolites and mechanical mixture of both (black), obtained by gravimetric analysis at 423K, B: linearization at short times.

IR spectroscopy was used as a complementary method to gravimetric analysis because it provides additional data on the interaction, orientation and environment of the molecules on the solid surfaces. Figure 2A shows the IR spectra of activated H-MFI, H-FAU and mechanical mixture of both. It exhibits band at 3606  $\text{cm}^{-1}$  assigned to bridging Brønsted acid

OH groups of H-MFI and the bands at  $3645\text{ cm}^{-1}$  and  $3545\text{ cm}^{-1}$  assigned to bridging Brønsted acid groups in H-FAU zeolite, the high-frequency (HF) and low-frequency (LF) respectively [5]. As expected from the choice of the composition of the mechanical mixture, each of three bands belonging to the two porous networks can be clearly distinguished. The band at  $3745\text{ cm}^{-1}$  is assigned to free silanol groups of both zeolites.

The fractional coverage of acidic OH groups interacting with isooctane was followed using the integrated intensity of the negative difference band at  $3606\text{ cm}^{-1}$  for H-MFI and  $3645\text{ cm}^{-1}$  for H-FAU zeolite. Figure 2B shows the difference spectra for mechanical mixture at 423 K. These spectra characterize the formation of hydrogen bonds between the OH groups of the zeolites with the isooctane probe, leading to negative  $\nu(\text{OH})$  band at  $3606$  and  $3645\text{ cm}^{-1}$  of H-MFI and H-FAU in the mechanical mixture, respectively and the broader positive  $\nu(\text{OH})$  band at  $3450\text{ cm}^{-1}$ . The OH groups of H-FAU zeolite were covered much faster than the OH groups of H-MFI. Figure 2C shows the fractional coverage of these acidic OH groups as a function of time for pure H-MFI, pure H-FAU and the mechanical mixture. The fraction of the OH groups for H-FAU zeolite interacting with isooctane was found higher than the corresponding fraction in H-MFI. The IR experiment for the mechanical mixture, gives two profiles of adsorption: the fractional coverage of OH groups in H-MFI (violet curve), which is close to the fractional coverage of acidic OH groups in pure H-MFI (blue curve), and the fractional coverage of the OH groups in the supercages of H-FAU (brown curve), which is also very close to that of the pure sample (red curve). These results show that infrared spectroscopy can allow distinguishing the diffusion in distinct, non connected porous networks in a mechanical mixture.

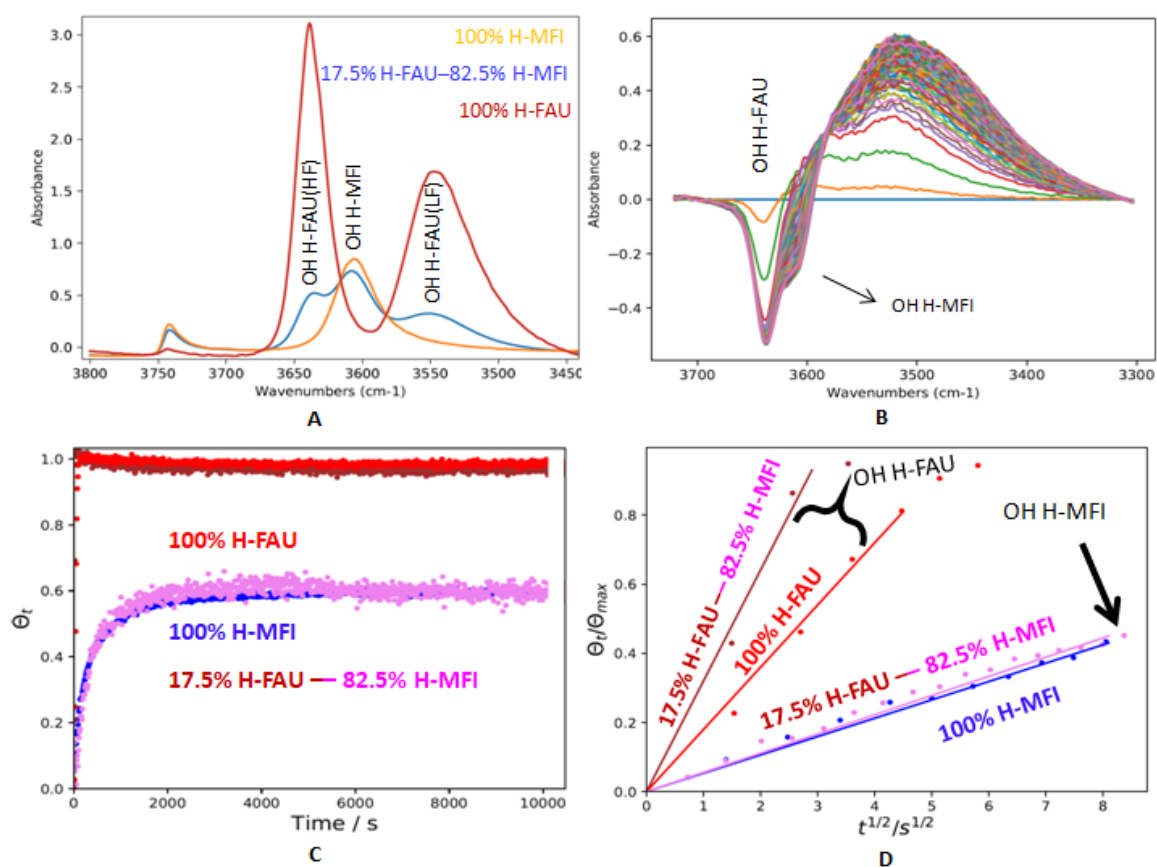


Figure 2. A: IR spectra of the OH groups of activated H-MFI, H-FAU and mechanical mixture of both. B: Difference IR spectra in the  $\nu(\text{OH})$  range of mechanical mixture of H-MFI and H-FAU zeolite. C: Fractional

coverage of acidic OH groups of H-MFI (blue), H-FAU (red) and mechanical mixture (17.5% H-FAU, brown and 82.5% H-MFI, violet). D: Normalized coverage vs square root of time in short time domain.

Fig. 2D shows the linear part of the normalized coverage vs square root of time for diffusion of isooctane in H-MFI and H-FAU, and the mechanical mixture. The initial slope of these curves allows assessing the characteristic diffusion time constant  $\tau^{-1} = D_{\text{eff}}/L^2$  [4]. For pure samples, we obtained  $D_{\text{eff}}/L^2 = 20.17 \cdot 10^{-4} \text{ s}^{-1}$  for H-MFI and  $D_{\text{eff}}/L^2 = 254.47 \cdot 10^{-4} \text{ s}^{-1}$  for H-FAU. In the mechanical mixture the diffusivities obtained for H-MFI OH groups ( $D_{\text{eff}}/L^2 = 20.77 \cdot 10^{-4} \text{ s}^{-1}$ ) and H-FAU OH groups ( $D_{\text{eff}}/L^2 = 314 \cdot 10^{-4} \text{ s}^{-1}$ ), are close to those measured for H-MFI and H-FAU respectively. The differences obtained in the case of H-FAU OH groups ( $+60 \cdot 10^{-4} \text{ s}^{-1}$  in the mechanical mixture) can be ascribed in part to a larger uncertainties on the determination of the initial slope (Figure 2D). Hence, these results show a good agreement of the values of diffusivity determined in each zeolite present in mechanical mixtures with pure H-MFI and H-FAU zeolites respectively. This confirms that IR technique allows distinguishing and assessing the diffusion properties of mechanical mixture of zeolites.

## CONCLUSION

In summary, diffusion measurement by infrared spectroscopy (using isooctane probe molecule and mechanical mixture of H-FAU and H-MFI zeolites) directly confirmed the distinction of the diffusivity and profiles of adsorption in each component present in mechanical mixtures of H-FAU and H-MFI zeolites. The present methodology has the potential to provide unique insights in the assessment of diffusion properties of complex micro-micro or meso-micro bimodal catalysts beds, such as micro-meso mechanical mixtures and hierarchical materials.

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