

Impact of steaming and shaping on the diffusion of zeolites by advanced IR spectroscopy methods

Luz Zavala², Françoise Maugé¹, Sylvie Lacombe², Philippe Bazin¹, Souad Rafik-Clement², Mickael Rivallan², Arnaud Travert¹

¹Laboratoire Catalyse et Spectrochimie, ENSICAEN, University of Caen, CNRS, 6 Bd Maréchal Juin, 14050, Caen, France.

²IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize – France.

Acidic MFI zeolite (H-ZSM-5) is widely used for multiple processes linked with catalysis, adsorption and separation. The outstanding performance of MFI zeolite is attributed to its unique structural and acidic characteristics. However, the intrinsic microporosity of MFI zeolites often leads to intracrystalline diffusion limitations when processing molecules with kinetic diameters greater than the pore size of zeolites [1,2]. Modifying the zeolite textural hierarchy offers larger pore dimensions for bulky molecules to reach active sites and/or exit as products. One way to overcome this problem is through the generation of mesopores in the zeolite. This can be achieved for example, through hydrolytic removal of Al atoms from their framework sites (dealumination) by steam treatment or steaming. Further, industrial catalysts (extruded bodies) contain besides the zeolite, other components like alumina, silica, amorphous silica alumina, or clays to guarantee the mechanical strength, in some cases dilute the active sites, improve hydrothermal stability and/or resistance to poisoning [3].

But using a binder can also affect the acidic and diffusional properties of the prepared zeolitic catalyst, due to the creation of binder / zeolite crystal interfaces, migrations of Si, Al atoms. In addition, steaming treatment of the zeolite before or after kneading/extrusion could result in very different zeolitic catalysts. This is where the motivation for our project lies, since the

information on the diffusion in catalysts and the pore connectivity is of vital importance for the technologies of interest for industrial applications.

With AGIR, qualitative and quantitative information about isooctane diffusion is obtained simultaneously by combining thermogravimetry and IR operando spectroscopy with online mass spectrometry. Isooctane was chosen as a probe molecule because of its kinetic diameter (0.62 nm), which is larger than the pore openings of unmodified ZSM-5 zeolite (0.55 nm). In this work we analyze the impact of steam treatment on the diffusional properties of the zeolites in powder form and in form of extruded bodies (Fig. 1). Besides the effect of the steaming treatment in zeolites, we have explored the influence of the nature of the binder and some preparation parameters of the extruded catalyst. Our results show two types of initial diffusion regimes in the extruded catalysts compared to the single initial diffusion observed for the powder zeolites. Finally, monitoring the uptake kinetics by AGIR is a promising analytical tool of zeolite-based catalysts.

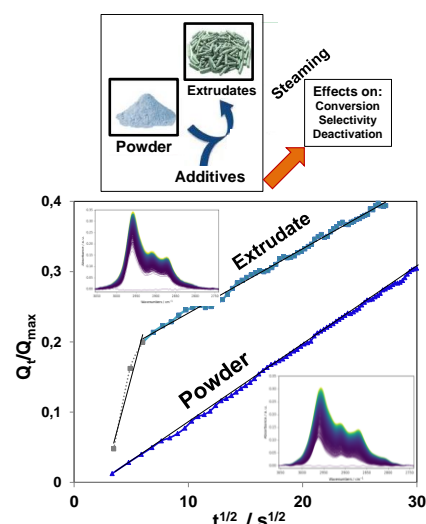


Figure 1. Isooctane uptake curves for zeolite powder and shaped zeolitic catalyst measured by AGIR.

References

- (1) Peng, P.; Stosic, D.; Aitlhal, A.; Vimont, A.; Bazin, P.; Liu, X.; Yan, Z.-F.; Mintova, S.; Travert, A. Unraveling the Diffusion Properties of Zeolite-Based Multicomponent Catalyst by Combined Gravimetric Analysis and IR Spectroscopy (AGIR). *ACS Catal.* **2020**, *10*, 6822–6830.
- (2) Holm, M. S.; Taarning, E.; Egeblad, K.; Christensen, C. H. Catalysis with hierarchical zeolites. *Catalysis Today* **2011**, *168*, 3–16.