In situ and *operando* FT-IR spectroscopy for plasma in catalysis

M. Rivallan, M. El Roz, F. Thibault-Starzyk

Laboratoire Catalyse et Spetrochimie, ENSICAEN, Universite de Caen, CNRS, 6 Bouleavard Maréchal Juin, 14050 Caen cedex

In situ FT-IR spectroscopy was performed in a plasma reactor (low pressure or DBD) for plasma pretreatment of the solid or for plasma-assisted heterogeneous catalysis. Several different reactors will be presented for recording infrared spectra of the gas between the electrodes, together with the spectrum of the solid placed between the electrodes for catalysis or for surface treatment processes. Time resolved spectroscopy allowed kinetic measurements, and some mechanisms of reactions on the solid under plasma were determined.

Recent FTIR spectrometers allow easy measurements on the whole of the mid-IR range at time resolutions up to 5 ns, they can be used to get real time information on plasma treatment of solids or of surface chemistry of solids under plasma.. In the following, a Glow Discharge Reactor was combined with step–scan FT-IR spectroscopy in order to follow excitation mechanisms of CO_2 in air plasma at the microsecond time–scale.[1]

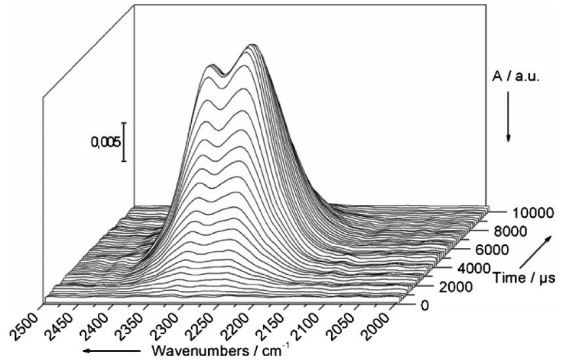

Fig. 1: *IR spectra evolution as a function of time recorded in the discharge zone composed of 15 vol.% CO_2 in air at 10 mbar for 10 ms corresponding to one plasma pulse at t = 0.*

FTIR monitoring of plasma treatment of a solid catalyst was applied to the calcination of metal containing zeolites (Fig. 2) [2,3]. It was particularly helpful in controlling the removal of templates or the conversion of the ammonium form of a zeolite into the acid form at low temperature, without detrimental effect on the morphology of zeolite nanoparticles. The role of water in the plasma was studied.

Catalytic reactions on solids can also be studied with real-time FTIR spectroscopy. The first example studied was isopropanol conversion by DBD on γ-Al_2O_3 catalyst [4]. The role of the solid surface and of the plasma in the reaction was established, and the reaction pathway was established.

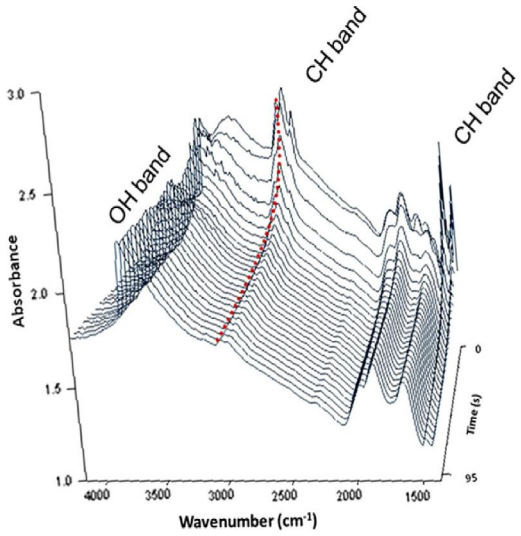

Fig. 2: *Evolution of the mid-IR spectrum of BEA zeolite during the removal of TEA template under oxygen plasma.*

References

[1] "Microsecond time-resolved Fourier transform infrared analytics in a low pressure glow discharge reactor", M. Rivallan, S. Aiello, and F. Thibault-Starzyk, *Rev. Sci. Instrum* 81 (2010) 103111.

[2] "Cold plasma as environmentally benign approach for activation of zeolite nanocrystals", M. El Roz, L. Lakiss, V. Valtchev, S. Mintova and F. Thibault-Starzyk, *Micropor. Mesopor. Mater.* in press DOI: 10.1016/j.micromeso.2012.03.003.

[3] "Plasma Synthesis of Highly Dispersed Metal Clusters Confined in Nanosized Zeolite", M. Rivallan, I. Yordanov, S. Thomas, C. Lancelot, S. Mintova, and F. Thibault-Starzyk, *ChemCatChem* 2 (2010) 1074.

[4] "Insights into the mechanisms of isopropanol conversion on γ-Al2O3 by dielectric barrier discharge", M. Rivallan, E. Fourré, J.M. Tatibouet, F. Thibault-Starzyk, submitted.