Operando transient EPR spectroscopy of N_2O activation and reaction on Fe-zeolites

D. Ferri[1], F. Buttignol[2,5], J. Fischer[3], A. Garbujo[4], G. Jeschke[3], O. Kröcher[1,5]

[1]Paul Scherrer Institut, Villigen, [2]Paul Scherrer Institut, VIlligen, [3]ETH Zurich, Zurich, [4]Casale S.A., Lugano, [5]EPFL, Lausanne

Control of N_2O emissions from stationary anthropogenic sources and novel fuel technologies is mandatory due to its large global warming potential. Catalysts based on Fe exchanged in silico-aluminates (zeolites) represent a major class of technologies currently used to remove N_2O from exhaust gases. While Fe-zeolite catalysts are active for this reaction, the nature of the active site remains debated because of the difficulty to obtain homogeneously dispersed Fe sites. Spectroscopy as a tool of characterizing the active sites during reaction suffers from the need to disentangle complex signals of species probably not involved in the reaction. In this contribution we show that electron paramagnetic resonance (EPR) spectroscopy coupled to transient experiments is able to provide information on the structure of the active sites of N_2O activation and reaction going beyond what was obtained so far.

We have analyzed a commercial Fe-zeolite catalyst comprising a number of Fe species of different degrees of agglomeration (monomers in different environments and clusters) by exposing it to pulses of N_2O in Ar, NO/Ar and $NO+NH_3+O_2$/Ar at 400°C while measuring products evolution with a mass spectrometer.

The EPR spectra of the catalyst exposed to N_2O at 400°C clearly showed that N_2O oxidizes all Fe species to Fe^{3+}. However, it is by repeatedly adding/cutting-off N_2O that only specific Fe^{3+} sites can reversibly activate N_2O and break the N_2-O bond. These species coincide with Fe coordinated in beta-exchange positions of the zeolite structure. Other species such as Fe coordinated to gamma-positions of the framework and also clusters can perform reversible Fe^{2+}/Fe^{3+} red-ox only when a reducing agent is added to the reaction, as in the case of the N_2O+NO and $N_2O+NO+NH_3+O_2$ environments. The work helps rationalizing the contribution of different Fe species in the mechanism of the simultaneous removal of N_2O and NO from exhaust gases that we have studied using X-ray absorption spectroscopy, EPR and infrared spectroscopy under identical experimental conditions to those shown here.

These results show that the transient nature of the experiments allows extraction of key mechanistic details that would remain otherwise hidden. This is even more important for a technique highly sensitive to the local environment of different Fe species such as EPR spectroscopy.