TITLE: “Self-sustained isothermal oscillations in the decomposition of N$_2$O over Cu-ZSM-5 zeolite”

HOME INSTITUTION: Politecnico di Torino. Supervisors of the PhD student in Torino: Raffaele Pirone, Barbara BONELLI and Edoardo GARRONE (Dipartimento di Scienza Applicata e Tecnologia, raffaele.pirone@polito.it).

HOST INSTITUTION 1: Ecole Nationale Superieure de Chimie de Montpellier (ENSCM). Supervisor: Gérard Delahay, Francesco Di Renzo

HOST INSTITUTION 2: CRF (Centro Ricerche Fiat, Orbassano, TO)

PROJECT DETAILS
Since the discovery by Iwamoto of its unique catalytic properties in DeNOx reactions, the copper exchanged ZSM-5 received a great attention by the scientific community, resulting in a huge number of papers published in international journals of several disciplines (catalysis, chemistry, physics and chemical and material engineering). The interest towards this material is related to the possible application in several DeNOx reactions, ranging from the SCR of NO with hydrocarbons, to the decomposition of nitrous oxide and the classical SCR with ammonia or urea. However, the great interest towards Cu-ZSM-5 was mostly addressed to the incomparable properties in the direct decomposition of nitrogen oxides, which has represented for a long time the most desirable DeNOx process, since it does not need the use of any reductant. Cu-ZSM-5 basically represents the only catalyst effective for this reaction at a reasonable temperature range (400-500°C), while no other similar formulation of catalyst (copper over other zeolites or mesoporous materials, or ZSM-5 exchanged with other transition metals) exhibits a comparable activity in NO decomposition.

The activity of the Cu-ZSM-5 in these processes is due to a series of peculiar properties joined with singular interaction with nitrogen oxides. One of the major characteristics of the system is the redox property of the exchanged copper in the zeolite that plays a very important role in the DeNOx function. More recently, the concept that catalyst reduction during the catalysis cycle occurs via nitrate species formation and subsequent decomposition with the formation of Cu$^{+}$ has been also reported [1]. Generally speaking, the formation of nitrate-like species over Cu sites seems to be necessary in a series of reduction processes towards N$_2$, and has also been observed in another singular phenomenon occurring on Cu-ZSM-5, namely the induction of a self-sustained and spontaneous N$_2$O decomposition with oscillatory rate [2-4]. The nature of these oscillations is purely kinetic, namely attributable to the reaction mechanism. Fanson et al. [4] proven that the concentration of nitrate species on the catalyst also follows an oscillatory pattern during oscillations of N$_2$O conversion, so to propose a mechanism that attributes a key role to nitrates formation and decomposition in the arising of oscillations.

Such an extraordinary singular phenomenon results largely un-explained, to date. Pirone et al. [5] showed that the co-presence of even trace amounts of NO together with N$_2$O quenches the oscillations and strongly increase the N$_2$O decomposition rate, still suggesting an important role of adsorbed NOx on the entire phenomenon.

The relevance of studying such a phenomenon is related to the comprehension of mechanisms and properties of Cu sites in the search of explaining such unique deNOx performances that cannot be exploited in practical applications, due to the largely insufficient resistance of Cu-ZSM-5.

The PhD project represents a classical example of junction of surface chemistry, physical chemistry, chemical engineering and applied mathematics competence in order to achieve further knowledge. The idea is to start from the single lab-scale experiment (in an integral way) and going deeper and deeper into molecular level to understand the reasons of rate instability. A lab-scale microreactor will
be used to characterise the macroscopic phenomenon: the effect of several parameters must be acquired on both the existence of oscillation and on their properties (amplitude, frequency). *In situ* transient FTIR spectroscopy will be also used in connection with on-line gas analysis to give possible correlations between the surface species that are formed and the gas phase products in order to further understand the underlying mechanism driving the oscillations. On a parallel plan, mathematical modelling would try to translate into numerical code the kinetic scheme and assumptions attained.

**References**


