**Evaluation of transition metal heterogeneous catalysts deactivation in green chemistry processes**

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**1. Introduction**

In heterogeneous catalysis, at industrial level catalyst deactivation is translated in a reduced production in terms of conversion or selectivity losses. It is mainly compensated by optimization of process parameters up to a non-return point, where a shut-down of the full plant and catalysts reloading are mandatory. To this step, an expensive start up procedure follows. It is clear that this has a strong impact on process economics and as well on the catalyst market, accounting for 25 billion USD (datum 2019). Main deactivation mechanisms have been reviewed [1,2] and often parallel or multiple effects might play together, and, at the industrial level, this is mostly managed on experience basis. Chemical deactivation includes both the reversible and irreversible poisoning due to traces molecules or elements present in the flue gas or coke formation; physical deactivation includes fouling while thermal deactivation includes sintering and loss of active phase (i.e. vaporisation, solid state reactions and loss of surface sites due to secondary reactions). Mechanical deactivation is mainly due to attrition or erosion phenomena. In the frame of development of green industrial chemistry processes, the challenge is not only to develop catalysts or processes but also to investigate catalysts deactivation for key-challenge catalytic processes i.e., ethanol dehydrogenation [3] and/or oxidative dehydrogenation to acetaldehyde [4,5], CO2 hydrogenation to CH4 [6] and fuels or even S- poisoning over Ni catalysts [7] for green hydrogen production or in hot syngas cleaning after biomass gasification.

**2. Methods**

Experiments were performed on home-made synthesized catalysts by choosing suitable synthetic procedures and evaluating not only the preparation in terms of performances but also on the improvement in deactivation. Among suitable supported catalysts, abundant metal-based catalysts are certainly of interest and we will focus mainly on Co-, Ni-, Mo- and Cu- catalysts developed for mentioned reactions and extensively characterized both as fresh and after catalysis experiments by means of XRD, FE-SEM, FT-IR, UV-vis-NIR and TP techniques. Catalytic experiments have been performed in laboratory scale plants with the parameters reported in [3-7]. Online analyses have been performed by means of FT-IR spectroscopy by allowing the evaluation of concentration profile as a function of time. Mathematical fitting of concentration profile has been carried out to evaluate the activity factor and characteristic deactivation time upon which steady state is reached.

**3. Results and discussion**

For Co- based catalyst upon CO2 hydrogenation an effect of preparation procedure and methane production has been observed upon both the precursor and the exposure of the catalysts at high temperature, that exhibit a reduction in methane production and a remarkable increase in CO one, suggesting the existence of two independent sites and the killing of methanation one in reactant stream. Moreover, cubic cobalt particles rapidly become deactivated by encapsulating carbon according to their high activity in favoring the formation of C-C bonds [6,8]. In the case of ethanol dehydrogenation to acetaldehyde, Cu-based catalysts mainly supported over an oxidic carrier with tailored acido-base properties are used i.e., ZnAl2O4 or MgAl2O4. In this frame, copper suffers of both sintering, occurring already at low temperatures, and of coke deposition. A typical experiment is reported in Figure 1, where a decay of acetaldehyde concentration and an increase in ethanol one can be clearly envisaged. In all cases, the mathematical fitting by using an exponential decay function allowed the evaluation of characteristic deactivation time, by helping the interpretation of obtained results. As well, in an analogous way, the behavior of Ni- based catalysts in CO2 hydrogenation to methane will be presented and extensively discussed.



**Figure 1.** Ethanol Dehydrogenation over Cu/ZnAl2O4 catalyst - concentration of ethanol (black) and acetaldehyde (grey) as a function of time and temperature

**4. Conclusions**

Catalyst deactivation has been observed and evaluated over several transition metal materials devoted to the exploitation of green industrial chemistry processes. All the results will be widely discussed in the frame of the understanding of catalysts deactivation and possible strategies to reduce it.

**References**

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