

Oxidative DeHydrogenation (ODH) of propane over mesoporous $\text{VO}_x\text{-SiO}_2$ catalysts with comparable vanadium content (V-SBA-15 and V-MCF ca. 2.5 % by weight) also depends on the Brønsted acidity of V species, as measured by IR spectroscopy (Fig. 4A) [54-56]. Indeed, Brønsted acidity seems to be negatively correlated with the selectivity to propene, since stronger Brønsted acid sites favour the formation of CO_x and other by-products (Fig. 4B) [57,58].

Moreover, higher selectivity to propene (selective oxidation product) was obtained over V-MCF as compared to V-SBA-15. This behaviour was related to the different porous network of the two catalysts: the structure of MCF, featuring a 3-D network with ultra-large cells (20-40 nm), favours molecular diffusion along each direction (= lower residence time), unlike cylindrical channels of SBA-15 (3-6 nm) occurring in one dimension mainly (axial diffusion). On the other hand, a non-porous sample prepared by flame pyrolysis (V-SiO_2), exhibited worse performances than mesoporous systems, confirming the important role of mesoporosity in oxidation processes [54-56].

Therefore, multiple causes affect the catalytic performance of redox systems, having ensembles of atoms (ions) and electrons mutually interacting in dynamic active networks. On the other hand, both structural and chemical complexity are closely related in transition metal oxide catalysts operating through a Mvk mechanism and this further suggests that such redox catalysts are very sensitive to the reaction conditions.

Moreover, several studies revealed that oxidation reactions at solid surfaces may change their reaction mechanism as a function of temperature [47]. G.I. Golodets et al. [49] proposed a classification of the oxidation mechanisms as function of temperature, according to which the redox MvK-type mechanism takes place in the temperature range between 300 and 500 °C, being replaced at higher temperatures by radical processes in the gas-phase. Below about 100 °C oxidation reactions may occur through peroxidic mechanisms, in which adsorbed radicals are directly involved. Golodets also identified a “transitional” region at moderate temperatures (in the range between 100 and 300 °C), where complex surface re-oxidation mechanisms are involved and the latter should be responsible for the formation of total oxidation products [47].

All these findings revealed that self-organizing phenomena may occur at the surface of metal oxides during oxidation reactions. Their geometrical structures can be described by means of 3-polytopes taking place both in space and time. On the other hand, a fractal approach ($3 + e$ dimensions, where e represent the dimension of the boundary) is likely more appropriate to describe theoretically the dynamic active networks operating in metal oxide catalysts.

5 Concluding remarks

The principles of non-linear dynamics govern self-organization phenomena in catalytic reactions. The latter typically occur in open systems, far from the equilibrium conditions, and hence the resulting spatio-temporal phenomena can be described through non-linear differential equations, combining both the chemical kinetics and the diffusion processes.

Self-organizing phenomena in heterogeneous catalysis reflect different complexity structures, including the self-repair and reorganization of active sites, the mutual interactions between neighbouring sites, the mass transfer limitations (i.e. shape selective control), the dynamic active networks of “sites-joined”, and so on. Thus, the observed self-organization processes at catalyst surfaces are related to spatio-temporal structures, in which both the structural and chemical complexity are closely related to each other.

As a whole, the catalysis process results in a non-linear combination of distinct complexity structures and hence catalytic behaviours may appear with multicomponent systems, such as zeolites or transition metal oxides acting via redox MvK-type mechanism. This also suggests the possibility of having non-reproducible reactions, i.e. in terms of reaction pathways and products.

In agreement with the theory of hyperstructures, the catalyst acts as a hyperoperator computing a non-linear combination (namely multivalued operation, \circ) of different complexity structures.

During the reaction (= Hv-structure), the catalyst allows reactants (i.e. x,y) to be mapped into the class of polytopes (a subset $x \circ y$ of H_v). The hyperoperation is weak associative because different complexity structures (sets) contain n-polytopes as common elements. This allows the condition required for the existence of the Hv-structures to be satisfied. Polytopes, with any general number of dimensions, have been introduced to describe

the complexity of the geometrical structure that is the initial set of the action of hyperstructures. Therefore, the algebraic hyperstructures (namely H_v -structures) are fine as a model to describe the complexity of catalysis.

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