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Preface

Selectivity in catalytic oxidation: an issue or an opportunity for innovation?

The title of this volume "*The selectivity issue: a driving force for innovation in catalytic oxidation*" has been inspired for the guest editors by the scientific career of Prof. Ferruccio Trifirò, to whom the volume is dedicated on the occasion of his 65th birthday. The control of selectivity in catalytic oxidation, and understanding the possibilities for its improvement, have always been the central topics of his scientific investigations and of the message he transmitted to his numerous collaborators on the industrial and academic sides.

Selectivity is the key aspect in the industrial development of oxidation processes, usually more than activity itself. The economic potential of any improvement in this area is enormous. It may be recalled, for example, that the economic impact deriving from the expected selectivity improvements in the first seven and currently operating, largest scale petrochemical oxidation processes, is about US$ 1.4 billion, worldwide [1]. The possibility of commercializing one or another catalyst for these processes is often a matter of a few points in selectivity; and, as has always been underlined by Trifirò in his lectures, it is surprising how the selectivity in some commercial processes is still low (sometimes lower than 80%). However, on the fundamental research side, the relationship between activity and catalyst properties is often the only aspect investigated. It is not uncommon that the selectivity of catalysts is compared at different levels of conversion without taking into account the dependence of selectivity on conversion.

The dependence of selectivity on feed composition is also often neglected. The use of high hydrocarbon concentrations or, in contrast, the use of oxygen-enriched air are aspects well known in the industrial practice but under-estimated from the fundamental point of view. Ferruccio Trifirò was amongst the first academic researchers to emphasise the importance of this aspect, starting from his first review on the factors controlling selectivity in the catalytic oxidation on mixed oxides [2] to the recent two books published on selective oxidation [3,4].

The role of dopants in promoting selectivity of mixed oxides is another very important aspect for industrial oxidation catalysts. Over 30 years ago, Trifirò was already studying complex Fe–Mo–Te-oxides on silica for the selective oxidation of hydrocarbons [5], pioneering studies on the role of Te as a promoter of selectivity in oxidation and ammoxidation catalysts [6]. Understanding the relationship between catalyst properties and selectivity was also one of the central aspects of his investigations [7], starting from fundamental work on the role of metallyl moieties in mixed oxides [8,9] in determining the selectivity in partial oxidation of hydrocarbons. Other relevant aspects to be mentioned are the roles of:

- non-stoichiometry in the rutile structure and on the properties of Sb-based oxidation catalysts [10];
- synergetic Lewis acid sites—oxygen basic sites on the selective activation of alkanes [11,12];
- VO^{2+} sites in the performance of vanadium oxide on titania catalyst for *o*-xylene oxidation [13,14];
- competitive surface reactions (H-abstraction versus O-insertion), after the rate-determining step, in affecting the selectivity and nature of the products [15] (a generalized kinetic model for the hydrocarbon oxidation selectivity over oxide-based catalysts, was developed [16]).

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Trifirò was also among the pioneers in investigating the selective oxidation of alkanes:

- *n*-butane oxidation to maleic anhydride [17–19];
- *n*-pentane oxidation to phthalic anhydride [20,21];
- propane ammoxidation to acrylonitrile [22–24];
- alkane oxidative dehydrogenation to alkenes [25–27];
- isobutane oxidation to methacrylic acid [28–30];
- methane partial oxidation [31–34].

Most of these aspects are summarized in his seven ''k-eys'' for designing a catalyst for the selective oxidation of alkanes [35]:

1. presence of vanadium;
2. isolation of the active sites;
3. stability of the reaction products;
4. multifunctionality of the catalyst;
5. non-desorption of intermediates;
6. control of the relative rates of surface H-abstraction and O-insertion, and of redox versus acid sites reactivity;
7. formation of alkenes as reaction intermediates.

Selectivity is not only related to the activation of the alkane (as often supposed), even if this is the rate-determining step, but to the control of the consecutive surface reaction pathway. This key aspect of Trifirò's teaching not only gives a different perspective to the investigation of the surface reaction mechanisms in the selective alkane functionalization (''it is not only important to understand how the hydrocarbon is activated, but the entire pathway of reaction, transformation rates of the intermediates, and their surface lifetimes as well''), but it also opens several opportunities for the development of new processes having better atom economy, lower impact on the environment and reduced consumption of energy and raw materials. Avoiding the desorption of reaction intermediates (so avoiding the formation of by-products) was one key feature for successfully using less expensive n-butane as the raw material with respect to C4 alkenes, showing that the narrow and apparently more difficult route (alkane selective activation is certainly more difficult than alkene activation) may be the preferable one.

This overview of Trifirò's contribution to the selective oxidation field, which was always at the edge between industrial development and fundamental understanding, has centred on the concept of selectivity as an opportunity for innovation. It also demonstrates that selective oxidation is a research area with many possibilities for further development if lessons from the past are considered correctly.

For this reason, we invited researchers who have had, or still have, scientific relationships with Prof. Trifirò to provide contributions on the topic of *Selectivity in Oxidation* not only in order to look at recent progress in this field but also to give a vision of the past. In this issue of Catalysis Today, various aspects of the control of selectivity in catalytic oxidation are therefore examined (even though we are aware that a lot of research effort is still necessary to achieve really tuneable control of the selectivity), these including:

- identification of those reaction parameters which may allow the control of the reaction pathway in complex reaction networks;
- the role of phase co-operation and site isolation in selectivity;
- the role of catalyst morphological and structural features on the nature of the active sites, and how these features can be affected through specific preparations procedures;
- the influence of the support, of promoters or specific elements on the nature of active sites in multi-functional catalysts, and the prediction of active sites properties by computational methods;
- identification of reaction intermediates, often with in situ techniques, which may be precursors for the formation of undesired by-products;
- the use of non-traditional reactor configurations, in order to control the gas-phase composition and hence the catalytic performance;
- the role of gas-phase ''promoters'' on the control of catalyst surface properties.

In addition, the problems of (i) safety and of how the use of either hydrocarbon-rich or hydrocarbon-lean feedstock can affect the performance and of (ii) selectivity control, with the aim of minimizing CO_2 emissions into the environment, are addressed in review papers.

We believe that this presentation of Trifirò's scientific profile, even though short, demonstrates clearly the link between current research trends in selective oxidation and past experience. We hope that it will be useful also as a lesson for young researchers, showing that more attention should be given to past research in relation to current knowledge derived from progress in this research field.

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