Account/Revue

Heterogeneous partial oxidation catalysis on metal oxides

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A B S T R A C T

This review paper presents an overview of heterogeneous selective ammoxidation and oxidative dehydrogenation (ODH) of light alkanes, particularly of ethane. The conversion of ethane to ethene is in great demand in the domestic and worldwide chemical industry. The review has been voluntarily restricted to metal oxide-type catalysts, as it is devoted to the *special issue honouring Edmond Payen* and is based on 30 years of experience and discussions with pioneering scientists in the field. The main key factors, designated by Grasselli as the "7 pillars", have been emphasised: isolation of active sites, M−O bond strength, crystalline structure, redox features, phase cooperation, multifunctionality and the nature of the surface oxygen species. The main features and physical and chemical properties of solid catalysts for selective oxidation compared to total oxidation have also been emphasised. Several case studies have been presented to illustrate the concept and importance of the key factors of catalyst preparation and activation and of the catalytic atmosphere. Based on such analysis and recent discoveries and process developments perspective views are also given.

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1. Introduction

Life would not exist without oxidation! Oxidation is extremely important, both from a scientific and a practical point of view [1−15]. In the chemical industry, the oxidation reaction is probably the most important process, playing a key role in numerous industrial, environmental and energy applications [16−32].

Most monomers and ~25% of all catalytic reactions are obtained by heterogeneous oxidation of hydrocarbons mainly over metal oxide catalysts, and even ~50% of bulk chemicals if one includes synthesis of NO (NH_3 oxidation over a Pt-based catalyst) and SO_3 (oxidation of SO_2 over a V-

based catalyst). For instance, C_2−C_8 hydrocarbons lead to monomers such as vinyl chloride, ethene oxide, acrolein, acrylic acid, acrylonitrile, methacrylic acid and methacrylates, maleic and phthalic anhydrides, etc. The majority of studies have focussed on olefin-selective oxidation, in particular propene to acrolein over bismuth molybdate-based catalysts and acrolein to acrylic acid/acrylonitrile over Bi and V molybdate-based catalysts by the SOHIO group as early as the 1960s [33], but also on light alkanes, such as C_2-, C_3- or C_4-activation by oxidative dehydrogenation (ODH) to olefins ($C_2^=$ to $C_4^=$), or carboxylic acids on different oxides, such as Bi molybdates or vanadates, metal ions exchanging heteropolyacids of the Keggin-type, etc. Direct alkane selective oxidation has drawn major interest in industry and academia [16,34−41]. For instance, direct oxidation of propane to acrylic acid/acrylonitrile on MoNbSb(Te)V−O, of butane to maleic anhydride on VPO

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catalysts, of isobutyric acid oxidative dehydrogenation to methacrylic acid on Fe hydroxyl-oxy-phosphates, etc., has led to industrial processes.

The activities in the area of oxidative dehydrogenation of alkanes started in the 1960s [42]. In 1961, the oxidative dehydrogenation of pentane and 2-methylbutane was reported and mentioned the importance of the nature of surfaces on conversion and selectivity [43]. Another example was reported on the use of cobalt molybdate to enhance the formation of butadiene from a mixture of butane and oxygen rather than from simple dehydrogenation [44]. A Sb-Mo oxide catalyst was reported to oxidise 2-methylpropane to methacrolein with 49% selectivity at 22% conversion, and propane to acrolein with 29% selectivity at 15% conversion using a mixture of alkane, air, ammonia, and water at 508 °C [45]. The new technology of catalytic oxidative dehydrogenation (ODH) may completely change the way some of the nation's most important organic chemicals are manufactured. The conversion of alkanes like ethane (a by-product of petroleum processing and present in natural gas) to olefins (ethene, propene, butenes, and butadiene) is in great demand in the domestic and worldwide chemical industry. The lower price of light alkanes in comparison to the corresponding olefins makes the dehydrogenation of lower alkanes an attractive industrial process. Alkenes are important feedstock for the petrochemical industry. The demand for olefins, especially ethene, is expected to increase significantly in the near future. Selectivity and atom efficiency are the key parameters for all of the chemical reactions [46–56]. A high selectivity is necessary for achieving a high efficiency in the use of raw materials, environement and energy [57–64]. The selective transformation by oxidative catalytic processes such as oxyhydrogenation of low molecular weight alkanes into more valuable products such as olefins or unsaturated oxygenates with adequate catalysts is still a challenging task due to the low intrinsic chemical reactivity of the alkanes which demands a high energy input to activate them. Dehydrogenation of alkanes to light olefins shows some major disadvantages, i.e., a high tendency to coking and consequently a short catalyst lifetime [65]. Transformations of hydrocarbons promoted by solid metals and their oxides play very important roles in the chemical industry with oil fractions, oxidation, dehydrogenation, isomerisation and many other processes of saturated as well as alkylaromatic hydrocarbons [66–84]. Metal oxides represent the most important families of solid catalysts for selective heterogeneous oxidation catalysis as active phases or as supports. The three main features of these oxides, which are essential for their application in catalysis, are: i) the coordination environment of the surface atoms; ii) the redox and, subsequently, acid–base properties; and iii) the oxidation states of the surface cations. A general feature of the selective oxidation reactions in heterogeneous catalysis which has appeared with the years is that the oxide surface could be considered as living, as in a breathing motion, to allow the Mars and van Krevelen mechanism to occur. This consideration of the oxide surface was inspired by the suggestion of Haber [85–87] shown in Fig. 1. Such a property was clearly shown for iron phosphate catalysts

used for isobutyric acid dehydrogenation to methacrylic acid (vide infra), implying that the oxide structure should be strong enough to allow the redox mechanism to occur without structural collapse such as $2PO_4^{3-} \leftrightarrow P_2O_7^{4-} + O^{2-}$, as schematised in Fig. 1.

The surface of the oxide may well be badly crystallised, i.e., amorphous in the sense of XRD, to facilitate the occurrence of the redox mechanism, although the surface should also reflect the underlying crystallised structure as shown, for example, for V_2O_5/TiO_2 catalysts by HR-TEM analysis [88], and for VPO catalysts in n-butane oxidation to maleic anhydride [89]. An oxide surface could be badly organised although the underlying bulk structure is well defined. Seven key factors, designated as pillars by Grasselli [90], have been proposed to be satisfied for selective oxidation reactions to occur, namely: i) nature of lattice oxygen anions: nucleophilic (selective) rather than electrophilic (total oxidation); ii) redox properties of the metal oxide (removal of lattice oxygen and its rapid reinsertion); iii) host structure (permits the redox mechanism to occur without collapsing); iv) phase cooperation in a multicomponent catalyst or supported catalyst (epitaxial growth and synergetic effects); v) multifunctionality (e.g., α-H abstraction and O-/NH- insertion); vi) active site isolation (to avoid too high lattice O surface mobility and thus overoxidation); vii) M—O bond strength (not to be too weak (total oxidation) nor too strong (inactivity) (Sabatier principle)). Point i) of the active oxygen species was discussed a long time ago in two review articles by Tench and Che [91] who have described different types of oxygen species. For the redox mechanism, one may write: $O_2 + e^- \rightarrow O_2^-$; $O_2^- + e^- \rightarrow O_2^{2-} \rightarrow 2O^-$. These oxygen species are more or less electrophilic, or nucleophilic in the nomenclature proposed by Haber [92].

2. Structural aspects of M_xO_y oxides

Structural properties of M_xO_y oxides confer specific selectivity in oxidation reactions that depend on redox couples $M^{n+}/M^{(n-p)+}$, length/strength/ energy of M—O bonds, anionic defects (vacancies or anion excess, in particular O^{2-}) and/or cationic (vacancies or cation excess) [93]. The surface and bulk mobility of oxygen species is also an important characteristic of the catalyst. Selective oxidation catalysts generally contain a transition metal cation such as Ti, V, Cr, Mo, and W, highly charged, small and polarising. In vanadyl (VO^{2+}) and molybdenyl (MoO_2^{2+}) oxo-cations, multiple bonds are formed between the cation and oxygen. V^{5+} cations (ionic radius of $r_i = 0.054$ nm) float in an octahedral environment of six O^{2-} ($r_i = 0.140$ nm) and forms a V=O bond to be more stable. The V···O bond in *trans* V=O is longer, and its binding energy is weaker. Thus, this oxygen may easily be withdrawn, and the V coordination becomes five. Another striking feature is that octahedral environments of VO_6 in V_2O_5 and in V_2O_4 are very similar. Compared to V^{5+}, O= V^{4+} and V^{4+}···O bonds are longer (from 1.58 to 1.64 nm) and shorter (from 2.78 to 2.70 nm), and the height of the octahedron changes very little. Therefore, at the first approximation, one may expect an easy e^- transfer: $V^{5+} \leftrightarrow V^{4+}$ or $Mo^{6+} \leftrightarrow Mo^{5+}$ couples ($r_i = 0.059$ nm et