The selective oxidative activation of light alkanes. From supported vanadia to multicomponent bulk V-containing catalysts

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V-containing materials have been proposed as active and selective catalysts in the selective oxidative transformation of C$_2$–C$_4$ alkanes to the corresponding olefins, oxygenates and nitriles. Although vanadium ions are generally assumed as the active sites in the oxidative activation of short chain alkanes, the coordination, the oxidation state and the environment of V atoms strongly influence both the catalytic activity and the nature of the reaction products. A comparative study on the catalytic behaviour of V-containing catalysts, i.e. metal vanadates, supported vanadium oxides, V-containing microporous/mesoporous materials and multicomponent bulk Mo–V–Te(Sb)–Nb mixed metal oxides, on the alkane oxidation is presented. The influence of the structure (including the V-coordination and V-environment) and the physico-chemical properties (especially redox and acid–base characteristics) of the catalysts on their behaviour in the selective oxidation of paraffins and alkenes is discussed.

KEY WORDS: activation of light alkanes by vanadia catalysts; selective oxidative oxidation of light alkanes.

1. Introduction

A strong research effort has been devoted in the past three decades to the development of efficient processes for the partial oxidation of hydrocarbons. More recently, the research on selective oxidation of paraffins have been directed to both the oxidative dehydrogenation of light alkanes (C$_2$–C$_4$) to the corresponding olefins and to the substitution of olefins by paraffins in well known industrial processes, i.e. selective (amm)oxidation to the corresponding α,β-unsaturated aldehydes, acids, nitriles and anhydrides [1–8].

At the moment, the only selective gas-phase alkane oxidation that has been commercialized is the oxidation of n-butane to maleic anhydride, using vanadyl pyrophosphate, (VO)$_2$P$_2$O$_7$, as catalyst (a maleic anhydride yield up to ca. 60% at a butane conversion degree of 80% is actually obtained) [8]. However, this catalyst seems to be not so effective in the oxidative activation of C$_2$–C$_3$ alkanes [9,10].

Table 1 shows comparatively the worldwide production of some of the most important olefins and partial oxidation products [11], being ethylene and acrylonitrile (ACN) the most important compounds as feedstock and chemical product, respectively.

Ethylene is mainly obtained from the non-catalytic steam cracking of saturated hydrocarbons (ethane, propane, naphtha or gas oil). The production of ethylene and other olefins by steam cracking depend on the composition of the feed, the hydrocarbon to steam ratio, the reaction temperature and the furnace residence time. Thus, yields of ethylene about 50% can be obtained from steam cracking of ethane, while yields of ca. 30% of ethylene and of 20% of propylene are generally obtained from steam cracking of naphta [12]. However, this process produces a variety of products (methane, diolefins or acetylene), which are costly to separate from the ethylene. In addition, steam cracking is a highly endothermic reaction (operating at reaction temperature of 850 °C) requiring complex cracking furnaces to supply the heat.

Catalytic dehydrogenation reactions are also used in the attainment of olefins with more than three carbon atoms, although it represents a relatively low percentage of the total production [11]. However, as it occurs in steam cracking, this is a highly endothermic reaction (operating at reaction temperature of 700–800 °C depending of the alkane fed), and the catalyst deactivates by coke formation. So, catalytic dehydrogenation is probably not an adequate process, especially in the case of ethylene production.

Nevertheless, the increasing demand of olefins has enhanced the number of studies on other possible processes for the production of olefins. In this way, the oxidative dehydrogenation (ODH) and the partial oxidation of light alkanes seem to be interesting alternatives to the actual industrial processes. The ODH reactions have several advantages over catalytic dehydrogenation and steam cracking: (i) the formation of water gives an overall reaction that is not thermodynamically limited in terms of conversion; (ii) they operate at lower reaction temperature (400–550 °C); and (iii) coke is not formed (in situ catalyst regeneration is carried out by O$_2$ during the reaction).

In addition to the direct conversion of paraffin to olefins raw material, the substitution of expensive olefin

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different catalytic systems and different reactions conditions [15]. The more efficient utilization of raw material has led to two separate oxidation stages in all commercial facilities. The interest of the development of that reaction can be concluded from the evolution of the number of patents published in the last years (Figure 1).

V-containing catalysts have received much attention in the last two decades, especially for alkane oxidation reactions. One special issue in Applied Catalysis [16] and several issues in Catalysis Today [17], in addition to several reviews [1–8, 18–22] have been devoted to the catalytic properties of vanadium based catalysts. In this paper, the most interesting selective alkane oxidation V-containing catalysts will be compared, with special emphasis in their use in the oxidative dehydrogenation of ethane and propane and in the selective (amm)oxidation of propane. It will be concluded that, in all cases, the coordination and aggregation of $V^{5+}$ species, the redox properties and the acid–base character of the catalysts, strongly influence the behaviour of these catalytic systems.

2. Metal vanadate and supported vanadia catalysts

After the publication of the pioneer papers by Kung and co-workers on the ODH of propane and n-butane over V–Mg–O catalysts [18, 19], a number of supported metal oxides and metal vanadates catalysts have been tested for the selective oxidation of light paraffins. Although the yield of olefin attained was lower than 30% on the best catalytic systems [18–22], basic studies have served to evaluate the key factors in the selective oxidative activation of light alkanes.

V–Mg–O mixed oxides were extensively studied during the last decade since they are among the most active and selective catalysts in the ODH of propane and n-butane [18–25]. Although, in this case, the selectivity

by a less expensive alkane as feedstock in selective oxidation processes have been drawing increasing interest from the chemical industry in recent years. This alternative could represent a breakthrough for the realization of shut-down economics. The fact that alkanes are generally environmentally acceptable because of their low chemical reactivity has provided incentives to use them as feedstock for chemical production [1].

Though the number of partial oxidation products from C$_2$–C$_4$ alkanes such as olefins and their corresponding epoxides, aldehydes, acids or anhydrides is relatively high, only a few numbers of reactions seem to be possible. According to Cassidy and Hodnett [13], if the activation of the weakest C–H bond in the reactant directs the reaction towards selective oxidation, cleavage of any bond in the selective oxidation products will result in lowering the selectivity. The reactivity of the reactant and the stability of the partial oxidation products under reaction conditions determine the feasibility of a selective oxidation process. Taking into account these considerations and in addition to the synthesis of maleic anhydride from n-butane, ethylene (from ethane), and acrylic acid (AA) or ACN (from propane) seem to have the best expectatives in the next years for selective oxidation reactions.

Ethylene is one of the most important petrochemical intermediates and feedstocks for the production of many different compounds (polyethylene, ethylene dichloride, ethylene oxide, ethylbenzene–styrene, etc). The worldwide production in 2004 was about 102.9 × 10$^6$ ton/year, while the growth rate of ethylene demand is estimated to be 4.8% per year [14]. Actually, it is obtained by steam cracking of ethane or naphtha and half of the annual worldwide production is used for the manufacturing of polyethylene [11].

Acrylonitrile and AA are important intermediates in Petrochemistry, with worldwide productions in 2003 of 4.27 × 10$^6$ and 2.02 × 10$^6$ ton/year, respectively [14]. They are used as monomers in the production of fibres, resins, adiponitrile, and emulsion and solution polymers. Actually, they are synthesized from propylene using mixed metal oxides catalysts [4–6, 15]. However, while ACN is prepared in a single step [3–6], AA is obtained in two stages giving first acrolein and then AA, using two

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<th>Olefins</th>
<th>Partial oxidation products</th>
<th>Production (year)</th>
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*aFrom ref. [11].

Figure 1. Variation of the number of patents on selective catalysts for the (amm)oxidation of propane to acrylonitrile: (●) MoVTe(Sb)NbO-based catalysts; (□) V50O-based catalysts; (△) other catalytic systems.