

Self-adapting vanadium oxide catalyst for the oxygen-assisted transformation of light hydrocarbons to CO_x/H₂ through combined oxidation and WGS reactions

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The oxidation of light alkanes is often studied by using catalysts made of supported vanadium oxide, or of mixed oxides in which V is one key-element, and the reaction is either aimed at the formation of the corresponding olefins (oxidative dehydrogenation), or of oxygenated chemicals. Examples include the ODH of propane and of ethane, and the (amm)oxidation of propane to acrylic acid or to acrylonitrile, and of ethane to acetic acid. In the case of ODH, it is generally believed that the formation of the olefin occurs through a concerted mechanism of olefin and water co-production, with a possible contribution of homogeneous reactions (or heterogeneously-initiated homogeneous reactions), when the temperature is higher than 500-550°C. The present work describes the catalytic properties of V₂O₅, either as such or supported, in catalyzing the transformation of propane either into chemicals, such as propylene, or into CO_x/H₂ mixtures. The contribution of the different reactions involved, e.g., oxidative dehydrogenation, dehydrogenation, coke formation, reforming and WGS, has been examined.

The reaction of propane oxidation has been studied in a flow-reactor, by co-feeding the oxygen and hydrocarbon stream over a fixed-bed catalyst; residence time was equal to 2 s. Under conditions which did not lead to the total oxygen consumption (oxygen was the limiting reactant under our conditions), the main products formed included oxygenates (mainly acetic acid), propylene, carbon dioxide and carbon monoxide; no molecular hydrogen was produced. However, if conditions were used which led to total oxygen conversion, the formation of oxygenates became very low and the selectivity to propylene decreased.

The selectivities to CO and CO₂ showed opposite trends; in the meantime, the formation of hydrogen considerably increased. The amount of hydrogen produced was by far greater than that corresponding to propylene formation (under the hypothesis that the main contribution to propylene formation under conditions of total oxygen consumption was catalytic dehydrogenation, rather than ODH), while it did correspond to the increase in the formation of CO₂. Thus, evidence was obtained that the CO and H₂O produced by propane oxidation in the presence of gas-phase molecular oxygen were transformed into CO₂ and H₂ in the fraction of catalytic bed which operated under anaerobic conditions. Other reactions which contributed to H₂ production were the formation of coke and of coke precursors (cycloalkanes and aromatics).

The data obtained demonstrated that the oxidation of propane over V₂O₅ and supported vanadium oxide under conditions which are usually employed for the ODH of alkanes (i.e., hydrocarbon-rich conditions), leads indeed to a variety of reactions which contributed to the hydrocarbon conversion. Relevant reactions are alkane ODH and oxidative fragmentation to oxygenates, but also catalytic dehydrogenation and formation of coke precursors, which become the most important under conditions of total oxygen consumption. Moreover, in the case of unsupported vanadium oxide, the formation of H₂ occurs by combination of propane oxidation to CO_x and H₂O (with low selectivity to propylene), followed by alkane dehydrogenation and WGS reactions in the anaerobic section of the reactor, to generate CO₂ and H₂. The latter reaction was catalyzed by reduced vanadium oxide, which developed in the fraction of the reactor which operated under anaerobic conditions.