

## **Methanol and Ethanol Oxidative Dehydrogenation (ODH) to the corresponding aldehydes on vanadium-based catalysts**

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Formaldehyde and acetaldehyde can be obtained from methanol and ethanol, respectively, by dehydrogenation, oxidation, and different industrial techniques have been developed for these processes in the past.

In the recent years interest in formaldehyde and acetaldehyde production by the oxidative dehydrogenation (ODH) of the corresponding alcohols is increasing strongly. The ODH of alcohols to aldehydes seems, in fact, to be a promising alternative route to the partial oxidations, occurring more simply in a single step and in tubular reactors, provided that high activities and selectivities can be achieved under mild conditions of temperature (140-250°C) and pressure (1 atm).

Although, supported vanadium-based systems have been found to be active and selective catalysts in promoting the oxidative dehydrogenation of both methanol and ethanol to formaldehyde and acetaldehyde, respectively. Despite of these different other catalysts are still preferred in the industrial field. This is probably due to the fact that vanadium oxide catalysts performances are strongly affected by the specific interaction between with the support. It is generally recognized that the support has a strong impact on the catalytic behaviour of these and other ODH reactions by favouring or inhibiting the aggregation of vanadium oxide on the surface and by allowing the V-O-support bonds to be more or less involved in the reaction. TiO<sub>2</sub>, in particular, strongly interacts with vanadium oxide, thus favouring the molecular dispersion of the active phase.

Apart from the role of the support, the importance of the preparation method on the final catalyst behaviour has been largely discussed in literature. At this purpose, the catalyst preparation by using the grafting technique has gained interest in the recent years as a route for obtaining well dispersed catalysts.

In this work, in order to evaluate the effect of the support and vanadium load on both activity and selectivity, a series of vanadia catalysts have been prepared by grafting different amounts of vanadyl alkoxide on different supports, such as: SiO<sub>2</sub>, TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub>. Moreover, in order to illustrate the influence of the preparation method on surface structures and dispersion, as well as on redox behaviour and acidic and catalytic properties, a series of supported vanadia catalysts have also been prepared by conventional incipient wetness impregnation with a solution of ammonium metavanadate. Prepared catalysts and supports have been characterised by using different techniques, such as DR-UV, DRIFT, XRD, Laser-RAMAN, and tested in the ODH of methanol and ethanol. In particular, we have studied the kinetics of both the ODH of methanol and ethanol on a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalyst prepared by grafting vanadyl triisopropoxide onto a support of silica coated with TiO<sub>2</sub> using a multi-step grafting procedure. We tested the kinetic behaviour of the catalyst in both the ODH reactions by varying the reagent concentration; the residence time; the temperature. The vanadium load, the acid and basic characteristics of the catalyst and the presence in the feed of reaction products such as water, formaldehyde or acetaldehyde have also been determined. A reaction scheme consisting of five reactions has been developed for considering the evolution with time of all the reaction products, namely: formaldehyde, formic acid and the corresponding ester in the case of the ODH of methanol; acetaldehyde, acetic acid, carbon dioxide, acetals, and diethyl ether in the case of the ODH of ethanol.