

## Valorization of Ethanol by Anaerobic Transformation over Vanadium Containing Catalyst

J. Velasquez Ochoa, A. Malmusi, F. Cavani.

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Italy

### Abstractt

Bio-ethanol is nowadays considered one of the key players in the new Bio-refinery scenario for the synthesis of chemicals, as an alternative to fossil-based building blocks. Ethanol can be transformed to a variety of compounds, such as ethylene, acetaldehyde, ethylacetate, butadiene and 1-butanol. Vanadium oxide based-catalysts are amongst the most studied systems for ethanol oxidation to acetaldehyde.<sup>[1]</sup> Here we report on the reaction of ethanol anaerobic disproportionation to equivalent amounts of ethane and acetaldehyde over Fe/V oxide-based catalysts, and compare the performance with the oxidative dehydrogenation of ethanol to acetaldehyde.

A systematic study of the catalytic behavior of a  $\text{FeVO}_4$  catalyst was performed under different conditions and compared with reference oxides  $\text{V}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ . It was found that

the alcohol is able to reduce the sample at  $300^\circ\text{C}$  in absence of  $\text{O}_2$  and even in presence of it but at higher temperature ( $400^\circ\text{C}$ ). This reduced sample has a catalytic behavior that is

similar to the one showed by the  $\text{V}_2\text{O}_5$  (after reduction), but Fe plays a role as a "stabilizer" of the reduced phase by directing the reduction towards a non-stoichiometric spinel form. In this type of spinel, vanadium is mainly present as  $\text{V}^{3+}$  whereas in the case of  $\text{V}_2\text{O}_5$  the reduction under the same conditions leads to a mix of  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$  and  $\text{VO}$  with prevalence of the latter. The "over reduced" vanadium species catalyze side reactions that increase the C loss whereas the Iron containing catalysts keeps the selectivity to both the alkane and the aldehyde slightly higher, reducing their further oxidation to  $\text{CO}_x$  and the formation of heavier compounds that poison the catalyst. As regards the mechanism, it was observed that product selectivities are basically independent of reaction temperature and conversion, confirming its formation in a single (and not consecutive) step. Moreover, the in-situ DRIFTS study showed the formation of surface OH species (due to ethanol adsorption) on the reduced samples and this might confirm that the key step is the adsorption of two ethanol molecules on vicinal sites whereas at the beginning (on the oxidised state) the dominant way of adsorption was probably dissociated as ethoxy to give afterwards acetaldehyde (by dehydrogenation). This study is important in order to better understand the mechanism that governs this reaction which can be exploited as a way to valorize bio-ethanol.