

# Oxidative Dehydrogenation of Ethanol to Acetaldehyde on Supported Vanadium Oxide

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## Introduction

Supported vanadium oxides have been widely studied as selective catalysts for many redox reactions such as oxidative dehydrogenation of alkanes to alkenes, oxidation of methanol to formaldehyde, ammoxidation of hydrocarbons, but details about the reaction steps and the site requirements remain unresolved [1-3]. Supported  $V_2O_5$  domains catalyze the oxidative dehydrogenation (ODH) of ethanol to acetaldehyde [4]. The increasing availability of ethanol makes this route a potential alternative to the Wacker process in current use for acetaldehyde synthesis, provided that high rates and selectivities can be achieved at modest temperatures (400-500 K) and pressures (1 bar) [4]. Ethanol is also a useful probe molecule to complement our previous studies of alkane reactions of realistic catalytic oxide surfaces. Ethanol provides the requisite oxygen functionality within the feed and hence enables assessment of the tendency of a catalyst to dehydration (to ethylene) versus dehydrogenation (to acetaldehyde).

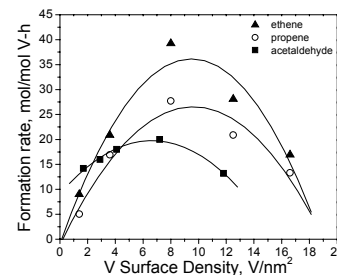
## Materials and Methods

$VO_x/Al_2O_3$  catalysts with various surface densities were prepared by incipient wetness impregnation of fumed  $Al_2O_3$  (Degussa AG; surface area  $119 \text{ m}^2/\text{g}$ ) with isopropanol (Aldrich, 99.99%) solutions of vanadyl isopropoxide (Aldrich, 98%). Samples were kept in a  $N_2$  flow within a glovebox overnight and transferred into a quartz reactor sealed with stopcocks. The impregnated samples were then treated at 393 K in flowing  $N_2$  for 1 h and at 573 K for 1 h; then, dry air was introduced and samples were held at 573 K for 1 h and at 773 K for 2 h. The structure of the catalysts was characterized by X-ray diffraction,  $N_2$  physisorption and Raman, UV-visible and X-ray absorption spectroscopy. Ethanol ODH rates and selectivities were measured in a quartz flow micro-reactor at 473-523 K. Infrared, UV-visible and X-ray absorption spectra during ethanol oxidation were used to probe the structure and oxidation state of V centers and the identity and reactivity of adsorbed intermediates.

## Results and Discussion

$VO_x/Al_2O_3$  catalysts form acetaldehyde with high selectivity at low temperatures. Rates and selectivity were unchanged during use ( $\sim 40$  h). Only acetaldehyde and diethyl ether were detected in the effluent stream at 473 K, while trace amounts of acetic acid, ethylene and  $CO_2$  were also detected at higher temperatures. The kinetic behavior of the catalysts was studied by varying residence time, reactant concentration, and V surface density. Measured kinetic dependences in  $O_2$  and  $C_2H_5OH$  partial pressures were 0 and 0.3, respectively, implying that ethanol derived intermediates are predominant on the surface and few reduced centers are present during steady-state catalysis, as shown by in situ UV-visible and X-ray absorption spectroscopic studies. In situ infrared spectra during ethanol oxidation and additional  $O_2$  adsorption on 10.5 wt%  $VO_x/Al_2O_3$  showed the presence of ethoxy species confirmed by the

bands at 2978, 2937, 2879, 1450, 1381, 1355, 1264,  $1170 \text{ cm}^{-1}$ . As the temperature was raised the band intensities of the ethoxy species decreased with concurrent increase of the band related to acetate species ( $1560 \text{ cm}^{-1}$ ). A highly selective  $VO_x/Al_2O_3$  catalyst, containing one theoretical polyvanadate monolayer ( $7.2 \text{ V}/\text{nm}^2$  10.5 wt%) was chosen because of its low reactivity in acid-catalyzed parallel reactions. Anaerobic transient experiments confirmed that  $C_2H_5OH$  oxidation to  $CH_3CHO$  requires lattice oxygen atoms and a reduction-oxidation cycle. Ethanol molecules deuterated at all positions ( $C_2D_5OD$ ) or only at the hydroxyl group ( $C_2H_5OD$ ) were used to probe the kinetic relevance of elementary steps involving ethoxide formation and H-abstraction from ethoxide during ethanol oxidation at 473 K.  $C_2H_5OD$  reactants gave no detectable kinetic isotope effect (KIE) (1.02), suggesting the formation of an ethoxide species is quasi-equilibrated. In contrast,  $C_2D_5OD$  gave a KIE value of 4.9, indicating that  $\alpha$ -hydrogen abstraction from surface ethoxide species is the kinetically-relevant step in acetaldehyde synthesis. ODH rates (per V-atom) are influenced by V surface density and by the support. ODH rates are low on isolated monovanadates prevalent at low surface densities



and reached maximum values at intermediate densities leading to the predominant presence of two-dimensional polyvanadate domains, and then decreased as  $V_2O_5$  crystallites with inaccessible V centers form.  $VO_x$  domains of intermediate size provide a compromise between  $VO_x$  reducibility and accessibility. The similar trend was found previously for formation of propene and ethene during the ODH of propane and ethane (Fig. 1). ODH rates and selectivities depend on the nature of the support, which also influences  $VO_x$  reducibility.

Figure 1. Product formation rates as a function of vanadia surface density on  $VO_x/Al_2O_3$  catalysts during the ODH of ethanol (4 kPa  $C_2H_5OH$ , 9 kPa  $O_2$ , 473 K,  $\sim 10\%$  conversion), ethane and propane [2].

## Significance

The present studies have provided a detailed picture of the ethanol oxidation on supported vanadium oxide. The results also demonstrate the relationships between the structure and reactivity of these supported vanadium oxide catalysts.

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