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## Mechanistic investigation of the ODH of ethane over a MoO<sub>x</sub> catalyst using in-situ techniques and Raman spectroscopy

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### Introduction

The understanding of the link between the observed chemistry during a reaction and the structure of the catalyst is essential for the development of reaction schemes and the operation conditions of a reactor (amount of catalyst, temperature, flow rate). However often the initial state of the catalyst is characterized (e.g. loading, oxidation state) and correlated to the catalytic performance<sup>1</sup>, omitting the possible change of a catalyst under the different reaction conditions along the catalyst bed. Here we will present an in-situ characterization of MoO<sub>3</sub> on  $\gamma$ -alumina as catalyst using the oxidative dehydrogenation (ODH) of ethane as sample reaction.

### Experimental

Using the incipient wetness impregnation method we prepared 30 wt% molybdenum oxide on  $\gamma$ -alumina (BET: 107 m<sup>2</sup>/g, stable under reaction). During the ODH of ethane spatially resolved mass spectrometry and thermocouple measurements allow to determine the gas phase composition as well as the temperature on each point inside the catalyst bed with micrometer resolution. These species and temperature profiles were combined with Raman analysis of several catalyst states inside the bed. The reactions were carried out at about 500 °C with GHSV of 520 h<sup>-1</sup> and 1040 h<sup>-1</sup>, a C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> flow ratio of 1 and an Ar dilution of 85%.

### Results

XRD and Raman analysis of the freshly prepared spheres show the presence of Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, mono- and polymolybdate species, but no MoO<sub>3</sub> as three dimensional crystalline phase. During the reaction the catalyst changes dramatically along the gas flow direction due to strong gas composition variations from an oxidative to a reductive gas atmosphere. A plot of the main reaction species and a picture of a quenched catalyst bed are shown in Figure 1 (GHSV: 520 h<sup>-1</sup>).

Here oxygen is converted after about 10 mm to more than 90 %. C<sub>2</sub>H<sub>4</sub>, CO and H<sub>2</sub>O are formed as primary products from the conversion of ethane on molybdate centers directly when the gas stream hits the catalyst. CO<sub>2</sub> instead is only marginally

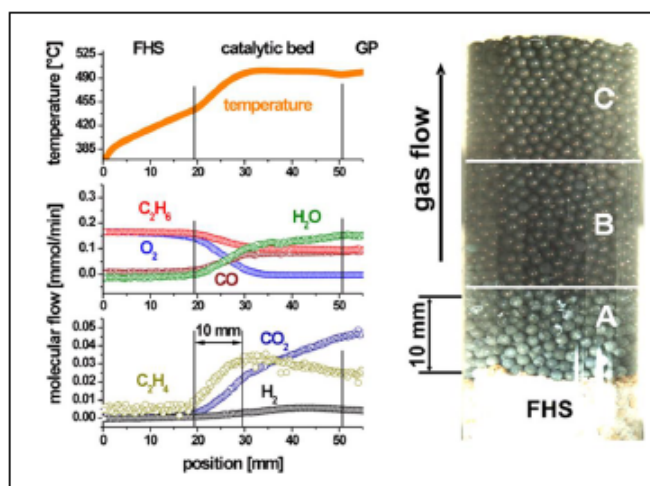


Figure 1: Catalyst species profiles along the reaction axis (left) and a look onto a quenched catalyst (right).

produced by total oxidation of ethane on not covered acidic alumina sites in a primary reaction<sup>2</sup>, but formed to a large extent as a secondary product from the further oxidation of ethylene. In this oxygen containing zone (Fig. 1 A, grayish spheres, electrical insulators) the catalyst spheres show Raman signals of Mo in the +VI state. After the oxygen is fully consumed the formation of ethylene stops and furthermore it is oxidized to CO<sub>2</sub> as this curve continuously increases with about ½ of its slope from the oxidation zone. The oxygen for this reaction comes from the catalyst, reducing it to MoO<sub>2</sub> (Fig. 1 B, violet spheres, high conductivity). The decreasing concentration of ethylene reduces the reduction of the catalyst towards the bed end, leading to partially reduced spheres (Fig. 1 C, black spheres, low conductivity, Mo present in +VI and +IV). A complete reduction to MoO<sub>2</sub> is likely after longer time on stream. This example shows clearly the necessity to avoid the complete conversion of oxygen to maintain the catalyst in the +VI state and to reach a high ethylene selectivity. Doubling the GHSV shifts the point of total oxygen conversion to the outlet, nearly fulfilling this criterion.

The usage of MoO<sub>3</sub> on  $\gamma$ -alumina in combination with the ODH of ethane illustrate explicitly that a catalyst structure changes under reaction and a correlation of the reactivity to the catalyst structure has to be drawn using in-situ characterization data.

<sup>1</sup> M. C. Abello, M. F. Gomez, O. Ferretti, Appl. Catal. A **2001**, *207*, 421-431.

<sup>2</sup> E. Heracleous, A. A. Lemonidou, Catal. Today **2006**, *112*, 23-27.