Combining Spatially Resolved Kinetic and Spectroscopic Measurements as Novel Research Tool in Selective Oxidation Catalysis

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Introduction

Selective oxidations of hydrocarbons are characterized by a network of parallel and consecutive reactions in which both the reactant and the desired intermediate are oxidized to CO_x. From a catalytic point of view these reactions follow a Mars van Krevelen type mechanism in which lattice oxygen of the transition metal oxide catalyst is involved in the product formation. Typically the initial catalyst is just a precursor from which the active catalyst is formed under reaction conditions. A careful reactor design is therefore necessary to maximize the yield of the partial oxidation product.

In the present contribution we present for the first time combined spatially resolved kinetic and spectroscopic data measured in oxidative dehydrogenation (ODH) of ethane to ethylene on a molybdenum oxide catalyst as model system. To demonstrate how the structure of the catalyst adapts to the declining chemical potential of oxygen along the flow direction and how ethylene is further oxidized by lattice oxygen, full O_2 conversion was realized in a packed sphere bed inside the tubular flow reactor. The structural development of the molybdenum oxide catalyst was followed by spatially resolved Raman spectroscopy.

Experimental

A model catalyst of 50 wt% MoO_3 on γ-alumina spheres of 1 mm diameter was prepared by incipient wetness impregnation. The ODH of ethane was carried out at atmospheric pressure in a dedicated spatial profile reactor [1]. In this reactor a fused silica capillary is moved along the flow direction of the tubular reactor sampling species into a mass spectrometer. Temperature and spectroscopic profiles are measured using optical fiber probes located inside the sampling capillary. A maximum reaction temperature of 520 °C was chosen to minimize the evaporation of MoO_3.

Results/Discussion

The catalytic data in Figure 1 show complete oxygen conversion at about 20 mm. The main oxidation products of ethane are carbon monoxide and water. Ethylene is formed as primary product as indicated by the non-zero slope of the ethylene profile at the entrance of the catalyst bed. CO and CO_2 show a zero slope at the entrance of the catalyst bed identifying them as secondary products. After gas phase oxygen is completely consumed ethylene is oxidized further by lattice oxygen to CO_2 accompanied by reduction of MoO_3 to MoO_2. Interestingly no CO is formed in this process and ethane is less prone to deep oxidation by lattice oxygen.
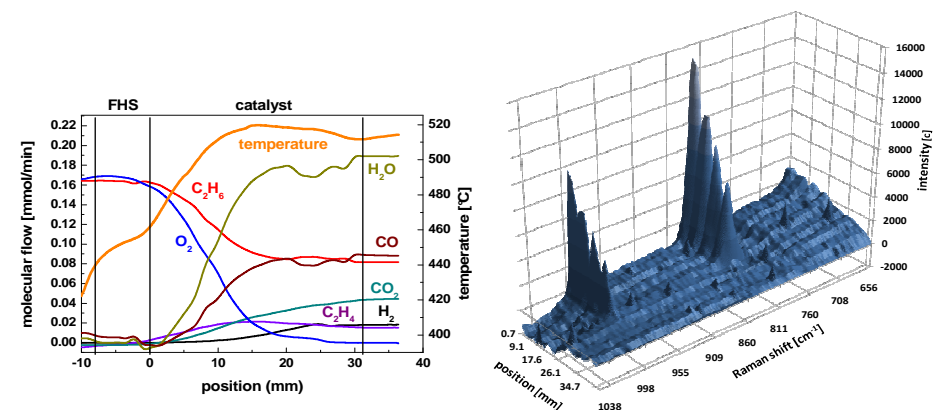

Figure 1. Left: In-situ kinetic data; Right: Raman spectra along the catalyst bed

The reduction of the catalyst can be followed by in-situ Raman spectroscopy. Spectra are shown in Figure 1, right diagram. Clearly visible are the two bands with the peak at 820 cm^{-1} for the Mo=O sym. stretch and at 995 cm^{-1} for the Mo=O asym. stretch vibration [2]. At about 20 mm inside the bed, where the oxygen conversion is nearly complete, the MoO_3 signal vanishes.

Simultaneous measurement of kinetic and spectroscopic data in selective oxidation catalysis allows insight into the mechanism of these reactions as demonstrated on this model system. The gained knowledge can be used to adjust catalyst and reaction conditions for optimum product yields.

References.

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