COMPACT PROFILE REACTOR FOR SPATIALLY RESOLVED KINETIC AND SPECTROSCOPIC MEASUREMENTS ON SOLID CATALYSTS

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Abstract

A novel compact profile reactor is presented. The reactor allows simultaneous measurement of concentration-, temperature- and Raman spectroscopic profiles through a bed of catalyst particles with submillimeter resolution. Profiles can be measured at temperatures up to 550°C and pressures up to 20bar. By correlating the spectroscopic and kinetic information the influence of catalyst dynamics on the catalytic reaction can be understood. The reactor has been applied to several exothermic and endothermic reactions such as the oxidative dehydrogenation of ethane to ethylene on vanadium and molybdenum oxide catalysts, the ethylene oxidation to ethylene oxide on silver and the dehydrogenation of propane to propylene on supported liquid palladium-gallium catalysts. Example data are presented.

Keywords

Profile Reactor, Catalyst Dynamics, Structure Activity Correlation, Raman Spectroscopy.

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Introduction

About 80% of all products our modern life is based on are made with the help of catalysts. The majority of them, in particular fuels and bulk chemicals are made in heterogeneously catalyzed reactions using solid catalysts. Solid catalysts are also used to clean emissions from mobile and stationary sources. Academic and industrial researchers around the globe optimize existing catalysts and search for new catalytic processes to meet current and future challenges. This business is competitive and often frustrating. Promising catalysts might not perform well outside the lab and improvements to established catalytic processes are incremental. One reason for this is that catalysts are dynamic. Catalysts change their structure and reactivity as function of local temperature and concentration conditions in the reactor. Fig. 1 shows color gradients of various catalysts operated in laboratory fixed bed reactors being an obvious manifestation of this dynamic behavior.

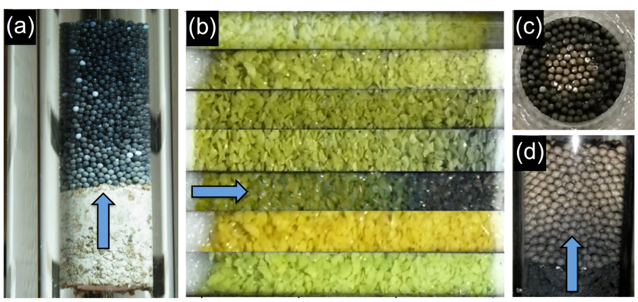

Figure 1: Color gradients in catalytic laboratory fixed bed reactors as an example of catalyst dynamics. Arrows indicate flow directions. a) $MoO_x/\gamma{-}Al_2O_3$ catalyzing the oxidative dehydrogenation of ethane $C_2H_6 + 1/2\ O_2 \rightarrow C_2H_4 + H_2O$ $\Delta H_{r^\circ} = -104.9\ kJ \cdot mol^{-1}$. b) $VO_x/\gamma - Al_2O_3$ catalyzing the same reaction as in a) at different inlet stoichiometries and temperatures. c - d) $Ni/\alpha - Al_2O_3$ catalyzing the dry reforming of methane $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta Hr^\circ = +247.3 kJ \cdot mol^{-1}$.

In this contribution a novel reactor type is presented that was developed to study the dynamic behavior of catalysts. The reactor is very compact. It fits on a laboratory bench, in a ventilated rack or in a fume hood. This so called **C**ompact **P**rofile **R**eactor (CPR) allows simultaneous measurements of sub-mm resolved concentration and temperature profiles through a fixed bed of catalyst particles for kinetic analysis. Furthermore is allows simultaneous Raman spectroscopic profile measurements to investigate the dynamic changes of the catalyst in response to the local concentration and temperature conditions. The reactor is designed as a flexible research tool for typical catalyst amounts synthesized in a laboratory and can accomodate catalyst beds up to 60mm in length and 4mm inner diameter. Profiles can be measured at temperatures up to 550°C and pressures up to 20bar. The reactor is fully automized, it can perform temperature programmed experiments, trigger gas chromatographs and mass spectrometers for product analysis and Raman measurements for catalyst spectroscopy. All transfer lines can be temperature controlled up to 200°C to avoid condensation of condensable species on the one hand and decomposition of temperature sensitive molecules on the other hand. The reactor was successfully tested for exothermic selective oxidation reactions on metal and transition metal oxide catalysts such as the oxidative dehydrogenation of ethane on supported vanadium and molybdenum oxide, the epoxidation of ethylene to ethylene oxide on silver or the endothermic dehydrogenation of propane to propylene on SCALMS catalysts [Taccardi et al. (2017)]. Several application examples will be presented.

Experimental

A picture and the functional principle of the compact profile reactor are shown in Figure 2. A fused silica reactor

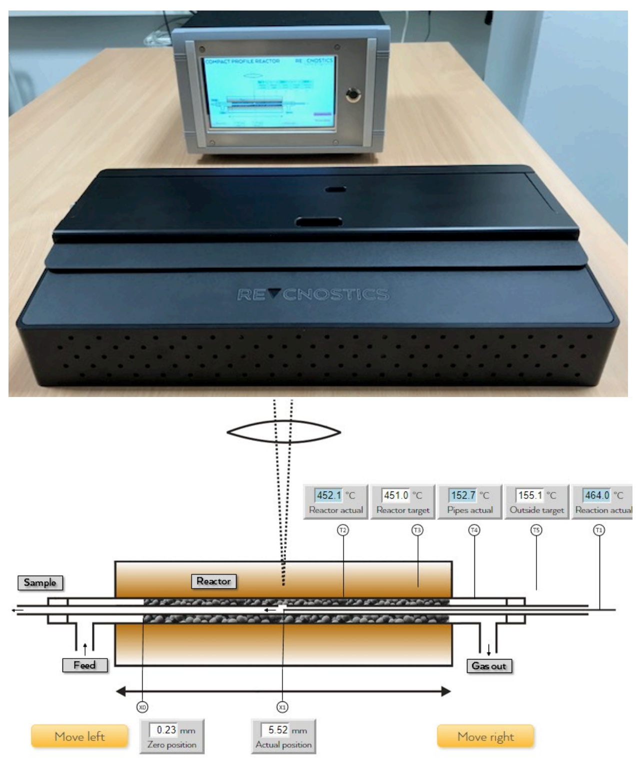

Figure 2: Functional principle of the compact profile reactor.

tube of 6mm OD and 4mm ID is filled with catalyst particles to form a bed up to 60mm in length. The reactor tube is mounted inside a heating zone and can be heated to target temperatures up to 550°C. For a flow of inert gas an isothermicity of +/- 1K over the length of the catalyst bed is reached. A thin fused silica sampling capillary (0.7mm OD, 0.5mm ID) is fixed in space and runs through the center of the packing. A small fraction of the reaction mixture is extracted from the catalyst bed through a tiny laser drilled side sampling orifice in the wall of the central capillary. Depending on reactor pressure the orifice diameter varies between 10 and 200 micrometers. The gas sample is guided to an analytical instrument (MS, GC) for quantitative analysis. Temperature or spectroscopic probes can be inserted from either side of the capillary and are tip aligned with the orifice. To measure the gas temperature a thermocouple can be used. The sampled gases flow around the thermocouple tip and the gas temperature is measured. To measure the catalyst temperature a pyrometer fiber can be inserted in the sampling capillary. The fiber picks up thermal radiation from the catalyst and guides it to a ratio pyrometer for temperature measurement. To gather Raman spectra from the centerline of the catalyst bed a thin Raman optic sensor can be inserted into the sampling capillary [Geske et al. (2013)]. The Raman sensor irradiates the catalyst in the vicinity of the sampling orifice with an excitation laser, collects elastically and inelastically scattered light and guides the scattered light to a spectrometer for analysis. Any of the two sensor combinations thermocouple / pyrometer, thermocouple / Raman, pyrometer / Raman) is possible. In addition to measuring Raman spectra in the center of the catalyst bed, Raman spectra can also be measured through the reactor tube wall by focusing the laser light through a slit in the heating/insulation mantle. The reactor can be placed horizontally under a Raman microscope or vertically next to it for measuring Raman spectra on selected catalyst particles. To yield spatial profiles the reactor body as a whole is translated by a stepper motor with micrometer resolution along the sampling orifice. The position of the sampling orifice, the temperature measurement and the spectroscopic probe volume remain fixed in space. The reactor is fully automated and can process even complicated experimental campaigns including triggering of external analytical equipment. An open browser based interface allows remote access from any computer independent of the installed operation system and even operation from any tablet computer or smartphone.

Results and Discussion

Figure 3 shows concentration and temperature profiles for the oxidative dehydrogenation of ethane to ethylene on a $VO_x/\gamma\text{-}Al_2O_3$ catalyst. Also shown is a picture of the catalyst particles and Raman spectra measured at selected positions using an excitation wavelength of 532nm and 1mW. Up to 9mm inside the bed, the concentration profiles show a gradual conversion of C_2H_6 and O_2 to C_2H_4 and CO. Almost no CO_2 is formed. Temperature increases from 488°C at the bed entrance to 505°C at 9mm. At 9mm O_2 conversion increases by C_2H_4 combustion to CO and CO_2. The Raman spectra reveal a reduction of the VO_x catalyst seen by the decreasing intensity of the V-O-Al and V=O stretching vibrations at 890cm^{-1} and 1023cm^{-1} respectively. The catalyst reduction observed by Raman spectroscopy correlates with the changing color of the catalyst from yellow (V^{5+}) to greenish (V^{3+}).

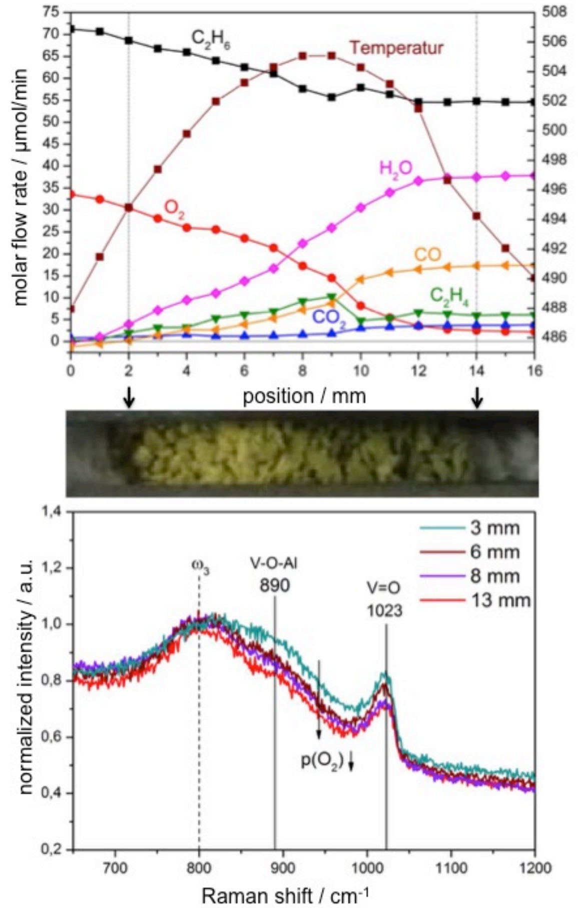

Figure 3: Top: Concentration- and temperature profiles measured for ethane ODH on a $VO_x/\gamma\text{-}Al_2O_3$ catalyst. Middle: Photograph of the catalyst bed under reaction conditions. Bottom: Raman-spectra of catalyst grains at selected positions.

The changing reactivity correlates with the reduction of the catalyst. In oxidized state the catalyst shows a higher selectivity to C_2H_4 than in reduced state. This example illustrates how catalyst dynamics influence the product distribution at the exit of a catalytic fixed bed reactor.

Acknowledgments

The authors would like to thank the Hamburgische Investitions- und Förderbank for financial support of the Reacnostics GmbH in their InnoRampUp Program.

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