Real-time spectroscopic control of a VPO catalyst for the selective oxidation of n-butane to maleic anhydride

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Introduction

Large-scale reactors loaded with catalytic solids are employed in a wide variety of chemical plants all over the world for the production of transport fuels and chemicals. Monitoring the chemicals that are leaving the catalytic process commonly controls these reactors. Once the product composition deviates from the desired one, process control actions are taken to correct for this change. A better approach is to on-line monitor the physicochemical phenomena of the catalyst material taking place in the reactor by means of in-situ spectroscopy and to develop an "expert system" based on such spectroscopic measurements. With such expert system it should be possible to make a corrective action once a spectroscopically visible change occurs in the catalyst material.

In this work, we illustrate this concept of on-line spectroscopic reactor control for a vanadium phosphorous oxide (VPO) catalyst used in the selective oxidation of n-butane to maleic anhydride.

Experimental

A schematic of the used set-up is outlined in Fig. 1. It consists of an oven with two holes, in which Laser Raman light is directed onto the catalyst sample. On-line gas analysis has been done with a compact GC.

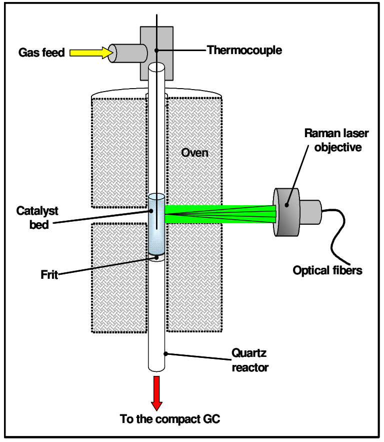

Figure 1. Schematic of the reactor set-up. The catalytic line consists of a 6 mm diameter quartz reactor tube with a special section made of optical quartz, that permits to focus the Raman light source. The catalyst is placed in the reactor as a packed bed supported on quartz wool just below the optical windows. The reactor is placed vertically in the center of a 15 cm long tubular oven block; a coated thermocouple is inserted in the catalyst bed to monitor on-line the catalyst temperature. The metal oven block has an 8 mm hole directed at the catalyst bed, used for focusing the Raman laser at the catalyst. The quantification of the product gas is possible with the on-line Interscience compact gas-chromatograph (GC) system equipped with two capillary columns. This GC is capable of performing gas analyses within 170 s.

Results and Discussion

The research consisted of two parts. In a first part, we have focused on the development of a catalyst monitoring system making use of in-situ Raman spectroscopy. We initially focused on the phase transformations between compounds with a vanadium valence of +4 (vanadium hydrogenphosphate hydrates [$VOHPO_4 \bullet xH_2O$] and vanadylpyrophosphate [$(VO)_2P_2O_7$]) and species with vanadium valence +5 (vanadylorthophosphate phases (α_I-, α_{II}-, β-, γ-, δ-$VOPO_4$, and $VOPO_4 \bullet 2H_2O$)). The $VOHPO_4 \bullet 0.5H_2O$ precursor, home made prepared in organic media, was transformed in situ under reaction conditions (400 °C, 30 ml/min, $He/O_2/C_4H_{10}$=77/21/2) to form the activated VPO catalyst (mainly [$(VO)_2P_2O_7$]). By alternating the reducing and oxidizing conditions it was possible to follow the appearance/disappearance of Raman peaks connected to phase changes (Fig. 2).

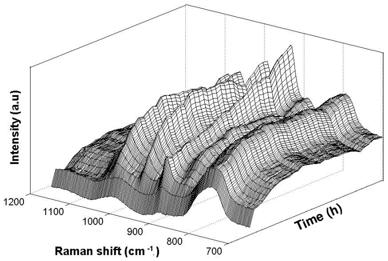

Figure 2. In-situ Raman spectra of a VPO catalyst as a function of reaction time (T = 400 °C; $He/O_2/C_4H_{10}$=77/21/2).

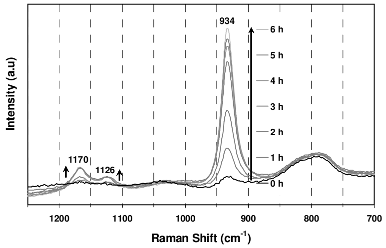

Figure 3. In-situ Raman spectra acquired at 700 °C as a function of time, during the formation of a pure $(VO)_2P_2O_7$ phase.

To be able to identify the components, references phases of [$(VO)_2P_2O_7$], β-$VOPO_4$, γ-$VOPO_4$, and $VOPO_4 \bullet 2H_2O$ were prepared under well-defined conditions starting from their molecular precursors. Their formation was continuously followed by Raman spectroscopy as shown in Fig. 3 for the [$(VO)_2P_2O_7$] phase, where the relative peaks at 1170, 1126 and 934 cm^{-1} increased with time.

In a second part of our research, based on this spectroscopic knowledge we have developed an expert system to monitor on-line the dynamic transformations of the VPO catalyst. Making use of this on-line spectroscopic control system we have determined structure-activity relationships. Special attention has been paid to the V^{4+}/V^{5+} - containing phases as a function of O_2/butane ratio in the feed.

Significance

We have developed an on-line spectroscopic control system based on in-situ Raman spectroscopy, which enables us to automatically control the relative ratio of V^{4+}/V^{5+}-containing phases in a catalytic reactor by tuning the O_2/butane ratio in the feed.

Acknowledgements

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