Operando Raman spectroscopy applying novel fluidized bed micro-reactor technology

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Introduction and Objectives

Due to the usually low Raman cross sections of molecules or solids, high laser powers need to be applied in order to produce a well detectable signal. However, one inherent problem of applying high laser powers is the risk of laser-induced damages in the sample. A critical issue, in particular in the field of heterogeneous catalysis, is that laser induced heating may also lead to significant differences between the measured temperature given by the thermocouple in the reactor and the actual temperature at the measured point. In the case of *in situ* Raman spectroscopy applied to chemical reactions at solid-gas interfaces, such as in the field of heterogeneous catalysis it is of particular interest to know exactly the temperature where chemical transformations occur.

We have recently discovered a new technology to homogeneously fluidize particles inside a micro-reactor and conduct heterogeneous catalytic reactions with it, such that they can be monitored by *operando* Raman spectroscopy, without the drawback of laser heating/damage [1].

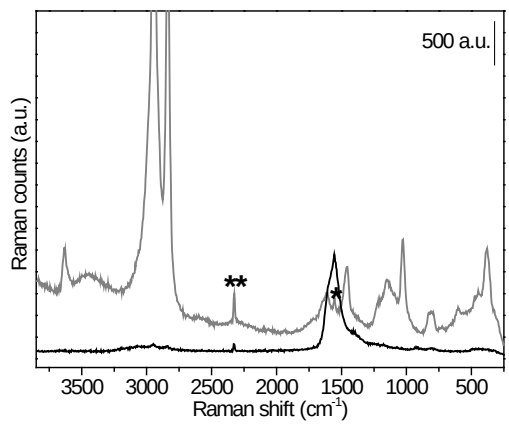
In this contribution we will illustrate the concept presenting results of two relevant case studies that have been performed with the new fluid-bed reactor:

> *Case A.* Investigation of the active phase in a commercial sulphuric acid catalyst (VK38, Haldor Topsøe) under realistic operation conditions (1 bar, 300 – 630 °C, 10% SO_2, 10% O_2, 80% N_2).
>
> *Case B.* Follow the formation of hydrocarbon molecules in the micropores of zeolites, during methanol to hydrocarbon reaction (MTH).

Results and Discussion

Raman spectra of a commercial sulphuric acid catalyst were recorded before and after switching the gas in the reactor at 380 °C from air to the reaction mixture (10% SO_2, 10% O_2, 80% N_2) and after a temperature step to 430 °C. Apart from the observed color changes of the catalyst from yellow-brown to dark green at 380 °C, the Raman spectra reveal a structural transformation, which has been interpreted as the transition from a polymeric vanadate to the well defined molecular structure of the $(VO)_3(SO_4)_5^{4-}$ ion, implying a reduction of $V^{(V)}$ to $V^{(IV)}$. Upon increasing the temperature to 430 °C further

structural changes are occurring, accompanied by an increase in conversion of SO_2. The main bands in the spectrum of the active catalyst have been assigned according to the literature and correspond to a mixture of mono- and dimeric $V^{(V)}$-sulphate species which fits well with the proposed active phases of Lapina *et al.* [2].



The great advantage of the new experimental set-up is reflected in **Figure 1**, where Raman spectra of methanol stream at RT on H-ZSM-5 sample with and without particle fluidization are reported. When the sample is fluidized (gray curve), the Raman spectrum of methanol, physisorbed or hydrogen bonded at the surface of the zeolite is easily recognizable, while in the lower energy part (1000-250 cm^{-1}) vibrational fingerprint of the H-ZSM-5 zeolite is visible. When the fluidization is stopped, the high energy laser (λ=244 nm) causes the decomposition of methanol, leading to the appearance of only one broad band centered at 1560 cm^{-1}, assigned to coke-like species deriving from methanol. We have investigated a number of different zeolite topologies and studied the hydrocarbon formation in the pores under MTH reaction conditions (while monitoring reaction products by MS). The structural differences in the hydrocarbon structures will be discussed and related to different zeolite pore geometries.

Conclusions

We demonstrate in two examples that fluidization of the catalyst particles is absolutely necessary to obtain the real structure of heterogeneous systems under operando conditions. The molecular structure of the supported molten phase in the sulphuric acid catalyst is very sensitive to changes in reaction conditions and the correlation with the catalytic data provided interesting new insight, enabling us to establish specific structure-activity relationships. The simultaneous monitoring of reaction products and intermediates in the gas phase and inside the micropores of the catalyst during MTH reaction provides unique details on the shape-selectivity of microporous materials. We are currently further developing the experimental set-up to extend the technique for combined *operando* UV-vis/IR/Raman spectroscopy. Some first results will be presented.

References

[1] P. Beato, WO2010/020320A1.

[2] O.B. Lapina, B.S. Bal'zhinimaev, S. Boghosian, K.M. Eriksen, R. Fehrmann, *Catal. Today* 51 (1999) 469.