IMPROVED EXPERIMENTAL SETUP FOR IN SITU UV/VIS/NEAR-IR SPECTROSCOPY UNDER CATALYTIC CONDITIONS

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Introduction

Diffuse reflectance spectroscopy in the UV to near-IR range is a suitable technique for studying electronic transitions of heterogeneous catalysts. In addition, the technique is potentially very sensitive for the detection of adsorbed reaction intermediates or side products, depending on the chromophores present in these species. Particularly useful is the combination of spectral information with simultaneously acquired catalytic data. In such cases one needs suitable spectrometer equipment to record any spectra with a high signal-to-noise ratio (i) at high temperatures (e.g. recording of spectra during the activation of catalysts) and (ii) under catalytic conditions in presence of low reagent concentration and/or high temperature.

Results and discussion

A commercial UV/Vis/near-IR spectrometer (Lambda 9, Perkin Elmer) was modified to measure reflectance in situ with improved signal-to-noise ratio from room temperature (RT) to 673 K [1].
The low signal level and thermal radiation could be resolved in the following way. The hot reactor cell was positioned at a distance of 12 mm from the integrating sphere to avoid its heating. The distance was bridged with highly reflecting ceramics to increase the part of light reflected into the sphere (1^{st} setup).
At higher temperatures the thermal radiation of the hot reactor is significantly stronger than the measurement light from the spectrometer itself. The requirements – large distance between integrating sphere and reactor cell, greater signal level, small analyzed area to reduce thermal radiation onto the detector, and a better arrangement of reactor cell and oven by a vertical position of powder samples – could be fullfilled by application of a specially formed light conductor made of quartz. In this light conductor the light is conducted to the sample and back into the integrating sphere by total reflectance. The additional mirror is necessary because only a part of internal totally reflected light can be totally reflected on this surface. The part of light that could leave the light conductor is thus reflected back into it (2^{nd} setup).
The improvement of the signal-to-noise ratio by the factor 4-5 is demonstrated by means of the following examples applying the 2^{nd} setup as compared with the 1^{st} :

1. UV/Vis/near-IR spectra of zirconia and silica up to 673 K [2].
2. n-alkane isomerization on sulfated zirconia [3]:
   n-C_4H_{10} at temperatures ≤ 373 K; n-C_5H_{12} at RT and low concentration (≤ 1kPa).

References

[1] M. Thiede, J. Melsheimer, Rev. Sci. Instrum., 73(2), 2002, 394.
[2] M. Thiede, J. Melsheimer, PerkinElmer Colloquium Optische Spektrometrie, COSP02, Nov. 2002 in Berlin.
[3] R. Ahmad, J. Melsheimer, F.C. Jentoft, R. Schlögl, submitted to J. Catal.