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TOWARDS BETTER AIR OVER SWITZERLAND: APPLICATION OF THERMAL ANALYSIS IN CATALYTIC RESEARCH

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The application of Thermal Analysis (TA) is very demanding for gas-solid reactions characterized by very small mass changes (smaller than ca. 0.1%). Such effects are within the range of those occurring due to buoyancy phenomena. The situation becomes even more complicated in the case of multistage reactions, simultaneous evolution of minute amount of gaseous products or when the processes occur only on the surface as e.g. during heterogeneous catalytic reactions. An increase of the TA sensitivity can be reached by application of hyphenated methods allowing analysis of the evolved gaseous products by much more sensitive techniques such as mass spectrometry (MS), Fourier Transformed Infrared spectroscopy (FTIR) or gas chromatography (GC) which, however, does not allow the continuous monitoring of the gas phase. All above mentioned techniques increase the sensitivity of the measurements by at least an order of magnitude compared to conventional TA experiments. However two important issues are still not satisfactorily solved: the quantification of the spectroscopic signals and the change of the integral mode of measurement, implying that the total course of the reaction is measured, from zero to full conversion.

Both problems can be solved by applying the pulse thermal analysis (PulseTA®) which is based on the injection of a specific amount of the gases or liquids into the carrier gas stream in coupled TA-MS or TA-FTIR systems and monitoring of changes in mass, enthalpy and gas composition in the differential mode. Calibration with known amount of injected internal standard (gas or liquid) allows fast and exact quantitative analysis of spectrometric signals originating from MS or FTIR. It also allows creating an user-own library which is important for quantitative interpretation of MS signals which often differ from the reference data as concerns intensity of fragmentation patterns. Quantitative interpretation of FTIR or MS signals gives access to the determination of evolved species at concentrations as low as $5 \cdot 10^{-7}$ mole i.e. in the range of 10-20 μg for the commonly used sample masses in the range of 10-50 mg.

The main feature of the PulseTA® applied in coupled systems as TA-MS and TA-FTIR is the identification and quantification of the gaseous products, which together with the thermal effects (DTA) and mass changes (TG), aids in interpreting the course of the reactions occurring only during duration of the pulse. This potential of PulseTA® allows simultaneous collecting of information concerning the gas and solid phases in transient mode what is very useful in catalytic research, especially in heterogeneous catalysis on solids.

The advantages of in-situ monitoring of gas-solid reactions in the catalytic systems will be illustrated using as examples the investigation of the catalytic processes occurring during NO_x storage on Ba/Pt/alox catalysts applied for cleaning automotive exhaust gases. Determination of the amount of active Ba-containing phases, their characterization and quantification, influence of the support on the storage properties, formation of barium nitrate and its reduction by propene- investigation of all these phenomena leads to the preparation of the catalysts possessing better efficiency in the removal of the nitrogen oxides from exhaust gases.

Some additional examples will illustrate the superior sensitivity of the PulseTA which exceeds the one of conventional TA by at least one order of magnitude.