# Application of a Simultaneous TGA-DSC Thermal Analysis System for High-Throughput Screening of Catalytic Activity

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ABSTRACT: We present here the use of a simultaneous TGA/DSC thermal analyzer as a high-throughput reactor system to measure after calibration the heat of reaction and therefore the catalytic activity of heterogeneous catalysts in a fast, reliable and reproducible manner. By coupling the gas outlet of the analyzer with a mass spectrometer via a heated capillary additional data can be acquired. As a test reaction the oxidation of carbon monoxide with synthetic air, using Hopcalite and several transition and noble metals as catalysts, was chosen. The setup presented allows the rapid sequential screening of about 70 catalysts per day.

KEYWORDS: *high-throughput screening, calorimetry, catalysis, TGA, DSC, heat of reaction*
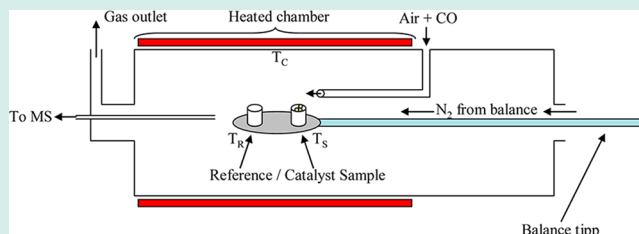
INTRODUCTION

Research and development in heterogeneous catalysis is still dominated by time-consuming single experiments, although an ever increasing variety of high throughput (HT) technologies are available and generally accepted.[1] Because of the infinite sampling spaces in heterogeneous catalysis there is still the challenge to develop new techniques that allow the user to check materials for their catalytic activity in a fast, easy and reproducible manner. While there already exists a diverse palette of established methods to check materials for their catalytic activity in a HT manner, most of them require high investment costs and are limited to very specialized applications.[1] Hence it would be beneficial when instead of highly specialized HT equipment generally available laboratory instruments, or equipment that can be used as multifunctional devices, are additionally used for high throughput screening (HTS). A parameter proportional to the catalytic activity of a material is the heat of reaction, which can be monitored using calorimetric HT methods like emissivity-corrected infrared thermography (ecIRT)[2,3] or parallelized microcalorimetry.[4,5]

Here we use a commercial TGA/DSC simultaneous thermal analysis system as a HT calorimeter to measure the catalytic activity of materials. To use a DSC system to measure catalytic activity has been proposed before,[6−9] but here we want to emphasize that it can be also used as a fast and reliable HT screening device. As a test reaction the oxidation of CO by synthetic air over a commercial Hopcalite catalyst was chosen. The reaction seems ideally suited due to the high heat of reaction of 283 KJ/mol,[10] the lack of side reactions and the traceability of the CO_2 by mass spectroscopy. In addition, because of the reductive properties of CO, the weight of the catalyst may change during the reaction resulting in a response of the TGA sensor. Since such a weight change is dependent on the specific nature and mass of the catalyst, the partial pressures of the gas phase and the temperature, it should only be used as

qualitative indicator in a sample library or as a source of extra information, but it may not be used as a quantitative measure for activity.

RESULTS AND DISCUSSION

Figure 1 shows a general scheme of the setup used for all experiments. In Figure 2, a photograph of the TGA/DSC unit with a fully loaded autosampler is depicted.
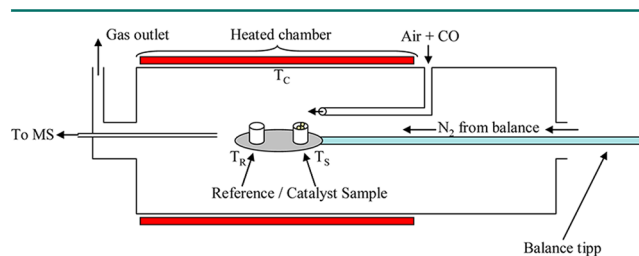

Figure 1. TGA/DSC setup with MS coupling. Three thermocouples measure the temperature of reference, sample, and oven chamber (T_R, T_S, and T_C).

In Figures 3 and 4 the temperature response and the MS-signal of different masses of Hopcalite catalyst in the TGA/DSC system for the oxidation of CO with synthetic air at $T_C = 120$ °C is plotted against time. The increase of T_S, as well as of the CO_2 MS signal correlate well with the amount of catalyst used, validating that the increase in temperature is caused by the heat of reaction evolved. With increasing mass of catalyst the particles are stacked above each other in the alumina vessels used. One may notice, that the correlation between the mass of
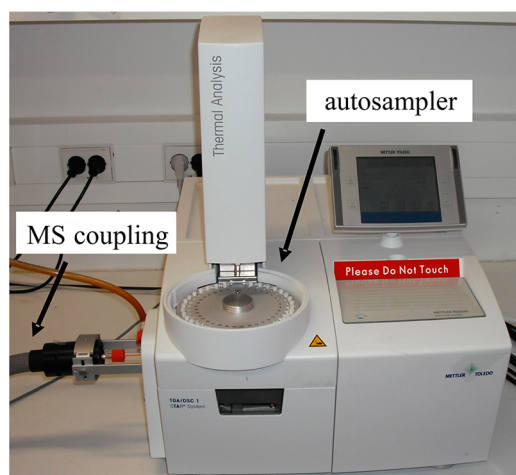
Figure 2. Image showing the TGA/DSC system with autosampler and MS coupling.
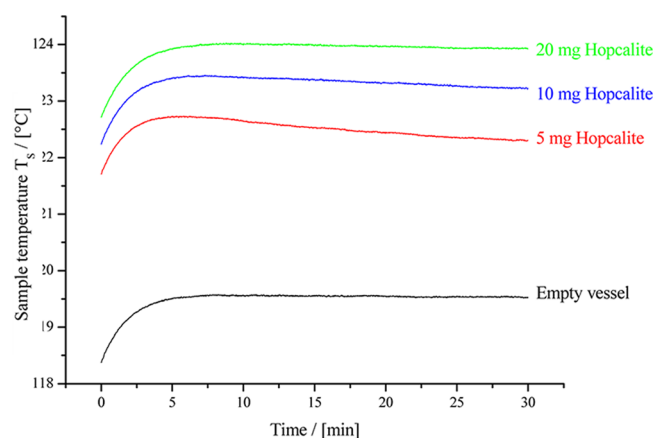

Figure 3. Experiment 1. Sample temperature T_S evolution at different masses of Hopcalite at constant oven temperature of $T_C = 120$ °C.
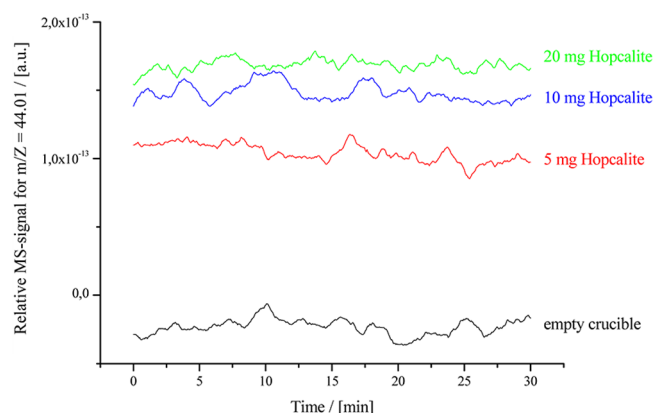

Figure 4. Experiment 1. CO_2 signal measured by MS at different masses of Hopcalite at constant oven temperature of $T_C = 120$ °C.

Hopcalite and the temperature increase in Figure 3 is not linear but rather asymptotically approaching a maximum temperature (see also Figure 8). This is probably caused by the largest part of the reaction taking place at the top layer of the catalyst hindering the particles at the bottom of the vessel from fully participating in the reaction. Also the increasing heat losses to the surrounding, due to particles at the bottom of the stack acting as a isolating layer above the temperature sensor, could

contribute to this effect. If one wants to compare activity of different catalysts, using this method, we would therefore recommend keeping either the weight or the filling level of the vessels constant.

The heat flux of this DSC system is calculated from the difference ΔT between T_R and T_S simply by multiplying this difference with the temperature dependent sensitivity $S(T)$ determined by calibration with enthalpy standards over the whole temperature range. Accordingly this heat flux responds to the parameters varied in the same way as ΔT. The sensitivity function $S(T)$ is characteristic for a specific instrument and depends, apart from thermocouple system, heating rate etc. also on catalyst mass and heat evolved. This sensitivity function takes into account that the sample crucible is connected to the thermocouple or the thermocouple array through a system of heat transfer barriers, so that not all heat generated is detected by the temperature sensor.

In Figure 5 the heat of reaction of different masses of Hopcalite was measured at different temperature levels T_C and
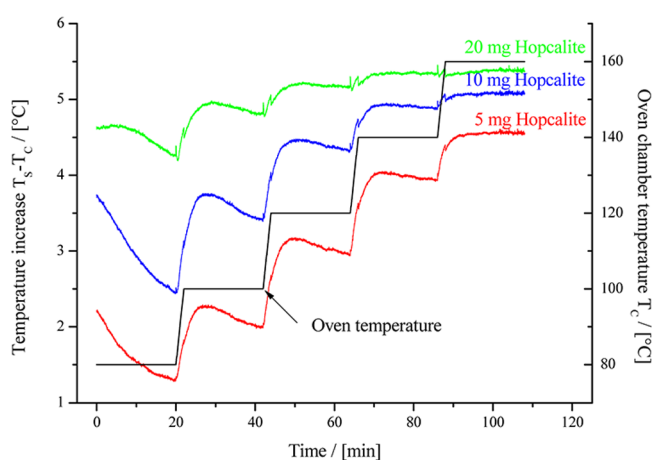

Figure 5. Experiment 2. The evolution of heat increases when T_C and the mass of catalyst used are increased. The oven chamber temperature T_C is scaled on the right y-axis, the temperature increase $T_S - T_C$ of the 3 catalysts is shown on the left y-axis.

plotted against time. As already shown in Figure 3 one can clearly see that the amount of heat produced is proportional to the catalyst mass. The second information that can be taken from the diagram is that the "deactivation behavior" of the catalyst, that is, the temperature reduction after reaching a maximum in the constant temperature phase of the program, changes with the temperature. Stable performance is only achieved at temperatures of 160 °C. In a paper by Brittan et al. and references therein, this deactivation behavior is also observed and explained by the reoxidation of the catalyst having a lower reaction rate than its reduction.[11]

Figure 6 shows that in addition to the increase in temperature the reaction-induced alteration of the thermogravimetric signal can also be monitored. In this case the relative weight loss of 11% is most likely caused by the reduction of copper(II) species in the Hopcalite system (see Szynkowska et al. for a TPR-TGA diagram of Hopcalite catalyst[12]). The T_{50} value defined as the T_C, where 50% of the overall mass loss on reduction by CO is observed at a given heating rate, increases with the amount of catalyst, while the step size in relative mass remains constant. As in the explanation for the asymptotic correlation between the Hopcalite mass and the heat signal we
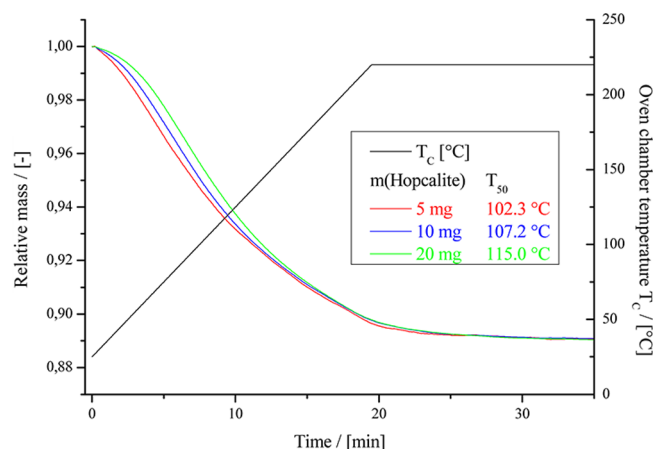
Figure 6. Experiment 3. The weight loss of Hopcalite as a function of time and mass of catalyst. The T_{50} value increases with the mass of Hopcalite used, while the step size in relative mass remains constant.

propose, that this increase of the T_{50} value correlates with the filling height of the particles in the crucibles which decreases the statistic chance of the CO molecules to reduce particles near the bottom of the crucible at increasing filling height. This would explain why at constant feed gas rates a longer time (resulting in larger T_{50} values) is needed to reduce all particles. The conclusion that has to be drawn from this is again that for comparative studies of different catalysts similar masses have to be used for the screening.

In Figure 7, the excess heat $(T_S - T_{S \text{ (emptycrucible)}})$ is plotted as a function of T_C. It shows that the ignition curve of the
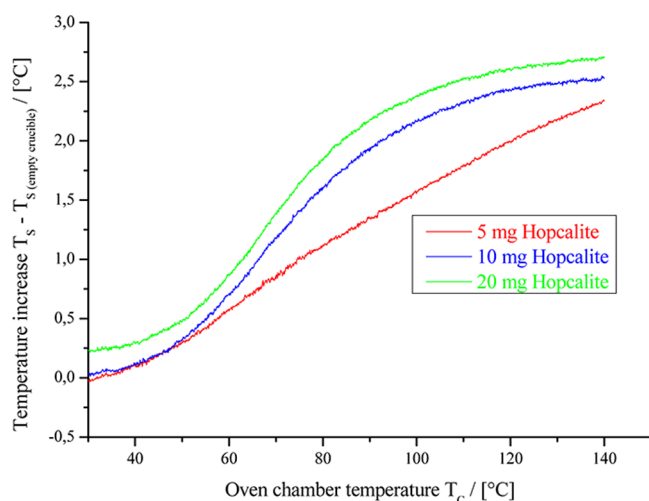

Figure 7. Experiment 4. Ignition curve related to the mass of catalyst measured at a heating rate of 10 °C/min.

catalysts can also be measured in a fast and reliable way using a TGA/DSC system. As expected with larger Hopcalite masses (meaning larger amounts of active sites) the ignition curve is slightly shifted to lower temperatures and the amount of heat evolved is increasing. By looking at the curves one can see that even at room temperature the Hopcalite catalyst is converting CO. With this type of measurement it should be possible to study and compare the ignition behavior of different catalysts.

Figure 8 shows the compiled results of experiment 5. For this fully automated "HT" run executed at $T_C = 120$ °C, the autosampler was packed with one empty crucible and 33 vessels
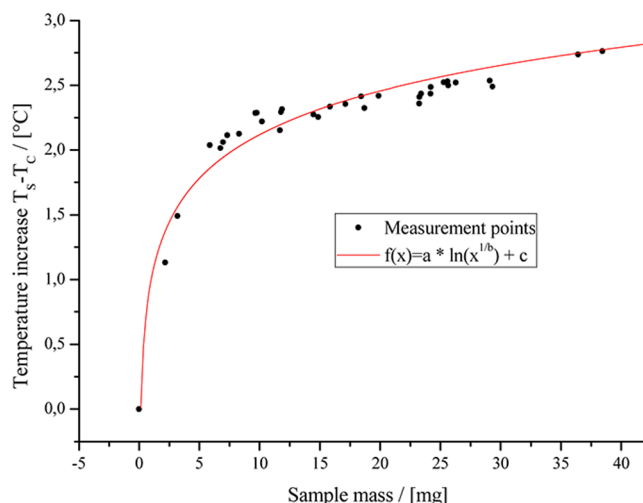

Figure 8. Experiment 5. Data analysis of a HT run at $T_C = 120$ °C. The increase in temperature correlates well with the mass of catalyst.

containing random masses of Hopcalite catalyst. In this simulated "HT" run the different masses of the Hopcalite catalyst (resulting in different amounts of active sites) are used to illustrate how a "HT" run using identical masses of catalysts with different activities should look like. Again the dependency between catalyst mass and heat evolution is clearly visible (average deviation between the fit curve and the measurement points = ± 0.1$_{08}$ °C), further emphasizing the reliability and reproducibility of the measurement. It is also shown, that the temperature increase per mass of catalyst $\Delta T/m$ meaning the resolution of the method is largest for small catalyst masses, indicating that for comparative studies small quantities of catalyst and small crucibles should be used. In this example an optimum is reached at about 10 mg of catalyst. The whole screening process including calibration and baseline correction took less than 12 h.

Figure 9 shows the compiled results of experiment 6a with 13 different materials as HT sample library. In this experiment, 10 mg each of the different materials were compared for their CO oxidation capability. The materials measured can be roughly divided into 3 groups: The highly active substances (1−3), the
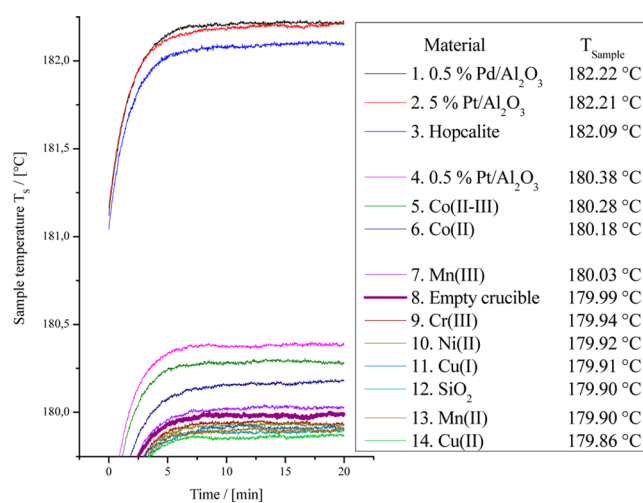

Figure 9. Experiment 6a. 10 mg of different materials were tested for their catalytic activity at $T_C = 180$ °C.

minor active substances (4–6) and the inactive substances (7–14). That some substances show a temperature slightly lower than that of the empty crucible (bold purple) can be explained by the substances in the crucible isolating the sensor from the heat flux of the oven chamber as confirmed by the measurement with sample 12, pure silica. The sensor measures a somewhat lower temperature when the crucible placed on it, is not empty, but filled with an inert (isolating) material like SiO_2. As the highly active catalysts 1–3 had very similar activities, it was likely, that their activities were limited by the CO content of the feed gas. Therefore, the activity of samples 1–3, 8, and 12 were measured again at higher gas flow rates (experiment 6b, not shown). Now it was possible to clearly differentiate among the samples. The activity ranking was 5% Pt/Al_2O_3 > 0.5% Pd/Al_2O_3 ≫ Hopcalite ≫ empty crucible > SiO_2.

■ EXPERIMENTAL PROCEDURES

All experiments were performed using a Mettler Toledo TGA/DSC1 heat flow system with a 34-fold autosampler and a high temperature oven HT1600. The system can be equipped either with a "DSC" or a "DTA" sensor revealing the same measuring principle (heat flow calorimetry), the two differing only in the number of thermocouple pairs (DTA = 1 and DSC = 3, each pair for sample and reference data accumulation) and thus in sensitivity. All measurements described here were performed with a DTA FRS2 sensor and 70 μL alumina crucibles. The DTA sensor was calibrated by the melting points and melting enthalpies of In, Zn, Al and Au at heating rates of 2, 5, 10, and 20 °C/min at N_2 flow rates of 50 mL/min. The balance was checked using the decomposition reaction of calcium oxalate monohydrate at N_2 flow rates of 50 mL/min. The gas flow was adjusted by Bronkhorst mass flow controllers. The reaction gas mixture consisted of 12 mL/min synthetic air and 1 mL/min CO, which were directly introduced into the oven and diluted with 10 mL/min N_2 to flush the balance. In the experiments 3 to 6, 40 mL/min N_2 were used. Water, whose temperature was set to 21 °C by a cryostat (Huber CC 415), was used as coolant.

MS data were acquired using a Balzers GSD 300 T2 mass spectrometer coupled via a heated fused-silica capillary (inner diameter 0.075 mm, SGE) to the oven chamber of the simultaneous thermal analyzer. Measurements were conducted in Faraday mode, the electronic zero-point adjustment was done at m/Z = 5.5. A scheme of the setup is shown in Figure 1.

Catalyst and gases have been supplied by C&CS (Hopcalite, sieve fraction 100–200 μm), Degussa (0.5% Pd/Al_2O_3), Acros (5% Pd/Al_2O_3), Alpha AESAR (Co_3O_4, 99.7%), Aldrich (0.5% Pt/Al_2O_3; CoO, 99.99%; Mn_2O_3, 99.999%; MnO, 99.99%), ABCR GmbH & Co. KG (Cr_2O_3, 99.999%; NiO, 99.99%; CuO, 99.9%), Fluka (Cu_2O), Merck (SiO_2, sea sand, extra pure), Air Liquide (N_2 of grade 4.8) and Praxair (synthetic air of grade 5.0 and CO of grade 2.3).

The following experiments have been performed: Experiment 1. Catalytic activity 1. The program consisted of gas stream equilibration, set point increase of the TGA/DSC system to 120 °C (T_C), insertion of a crucible into the oven chamber by means of a sampling robot and data acquisition for 30 min, beginning when the oven temperature has stabilized after the insertion of the sample again at 120 °C. Baseline correction was done by subtracting the data record of an empty crucible. 0, 5, 10, and 20 mg of a commercial Hopcalite catalyst filled into 70 μL crucibles were used as samples. The exhaust gas was analyzed by MS at the mass of the oxidation product CO_2 (m/Z = 44.01).

Experiment 2. Catalytic activity 2. As before, but T_C = 80 °C was used as starting temperature and this temperature was held constant for 20 min to equilibrate the analyzer. Subsequently the temperature was increased stepwise at a rate of 10 °C/min with constant temperatures at 100, 120, 140, and 160 °C for 20 min.

Experiment 3. Weight loss. As before, but T_C = 25 °C was used as starting temperature. Subsequently the oven was heated to 220 °C at a rate of 10 °C/min and this temperature kept constant.

Experiment 4. Ignition point. As in experiment 3, but 140 °C was used as end temperature. Instead of fresh catalyst Hopcalite prereduced at 220 °C in the reaction atmosphere was used.

Experiment 5. Simulated high-throughput run. As before, but setting the oven to a constant temperature T_C = 120 °C. Thirty-three 70 μL crucibles containing random amounts of Hopcalite catalyst and one empty 70 μL crucible were screened automatically with a sequential sample change after 10 min measurement time.

Experiment 6a,b. Comparison of different materials. As in experiment 1 but setting the oven to a constant temperature T_C = 180 °C. Thirteen 70 μL crucibles were packed with 10 mg each of different materials and screened together with one empty 70 μL crucible for back ground. The samples were automatically changed with a sequential sample changer after 20 min measurement time. For experiment 6b the gas flow rates of air and CO were tripled.

■ SUMMARY

It was shown that a TGA/DSC simultaneous analyzer as a stand alone application can be used as a powerful calorimetric tool in catalyst research revealing in situ gravimetric data of the catalyst in addition to the heat of reaction. By combination with a mass spectrometer (or any other analysis system as for instance a FTIR spectrometer, GC, etc.) a vast amount of additional data can be acquired. Apart from the use in catalysis as presented here, other HT applications like the measurement of heat evolution in crucibles filled with catalyst and liquid substrates or measurements of the heat/weight changes during gas absorption by storage materials should be realizable in a slightly modified setup.

During experiment 5, it was shown that the resolution of the method ($\Delta T/m_{catalyst}$) is best for small sample masses and small vessels. The TGA/DSC system needed about 10 min per sample to exchange a sample and to readjust the oven temperature. Taking this changeover time into account the system presented can screen about 72 materials for their catalytic activity in a 24 h period.

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Notes

The authors declare no competing financial interest.

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