

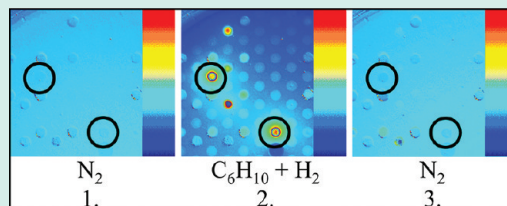
# Infrared Thermography as a High-Throughput Tool in Catalysis Research

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**ABSTRACT:** The so-called “emissivity corrected infrared thermography” (ecIRT) has been successfully developed and used to great effect in the field of combinatorial high-throughput studies in catalysis. A short introduction to the basics of ecIRT and the description of a typical setup is given. Research efforts from 1998 until present are summarized and selected publications with IRT applications in catalysis are highlighted. The last section of the article covers potential problems, which the observant may misinterpret as activity of the materials. The effects are classified and it is explained why they occur and what can be done to bypass them.

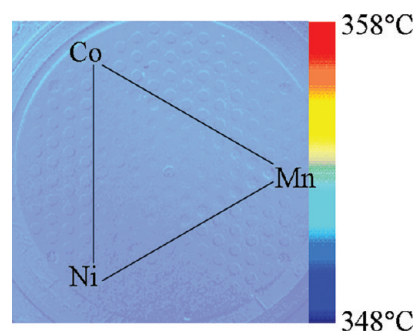
**KEYWORDS:** *emissivity-corrected infrared thermography, heat of reaction, heat of adsorption, false positive, false negative, high-throughput screening, influencing effects*



## INTRODUCTION

In recent years high-throughput experimentation (HTE) has become a widely used tool set in material sciences. The concept of modern HTE was first developed by Hanak<sup>1</sup> who questioned the “efficiency of the present approach to the search for new materials which consists of studying only one composition at a time”. He proposed that material research can be accelerated multiple-fold by the development of parallelized or very fast synthesis methods and analytical toolsets. Over the course of the last years a large and diverse palette of high-throughput techniques (HTT) to create and analyze material libraries were developed.<sup>2</sup> Well elaborated HTT are characterized not only by sample throughput and the use of combinatorial methods, but also by the data quality and their adaptability to different problems. One of these highly adaptable HTT is infrared thermography, which records temperature changes by area imaging. It has been applied to catalyst arrays already in 1996<sup>3</sup> but was suffering from poor temperature and spatial resolution. A refined method, the “emissivity-corrected infrared thermography” (ecIRT), was first published in 1998.<sup>4</sup> Infrared thermography in chemical applications records temperature changes, which correlate with the heat of reaction of a chemical process of interest, which in catalysis applications are related to reaction rate and thus catalytic activity. The energy released during a reaction (for example during the oxidation of methane on the surface of a catalyst, see Figure 2) disperses rapidly in the reaction products and the surrounding (in the aforementioned example, this would be the surface of the catalysts). Under invariable reaction conditions, the heat of reaction is proportional to the conversion and as the rise in temperature of the surrounding is proportional to the heat of reaction, an IR camera can be used to observe chemical processes with time and spatial resolution. The spatial resolution allows to observe not only one, but many samples in parallel. For example ecIRT can be used to quantify the activity of different catalysts by the

amount of heat evolved on their surfaces. The example in Figure 1 shows the emissivity corrected IR image of a catalyst



**Figure 1.** Emissivity corrected IR image of a catalyst library containing a  $\text{Co}_a\text{Mn}_b\text{Ni}_c\text{O}_x$  composition spread with an increment in composition  $\Delta a = \Delta b = \Delta c = 10\%$  heated in air to  $350^\circ\text{C}$ .

library in pure air at  $350^\circ\text{C}$ , while in Figure 2 the image of the same library with the same corrections, taken under reaction conditions in the presence of methane shows heat evolution, which is interpreted as relative heat of reaction. The most active catalyst here can be identified as a  $\text{Co}_{70}\text{Mn}_{20}\text{Ni}_{10}\text{O}_x$ .

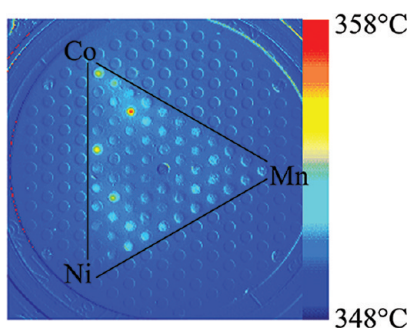
The proportionality between the emission of energy and the temperature of blackbody radiators is given by “Kirchhoff’s law of thermal radiation”, “Planck’s law”, and the “Stefan–Boltzmann law”.

Infrared images are obtained through 2D arrays of IR detectors in analogy to visual imaging in regular video cameras. The spatial resolution is determined by the number of IR detector pixel in the array. For the evaluation of information

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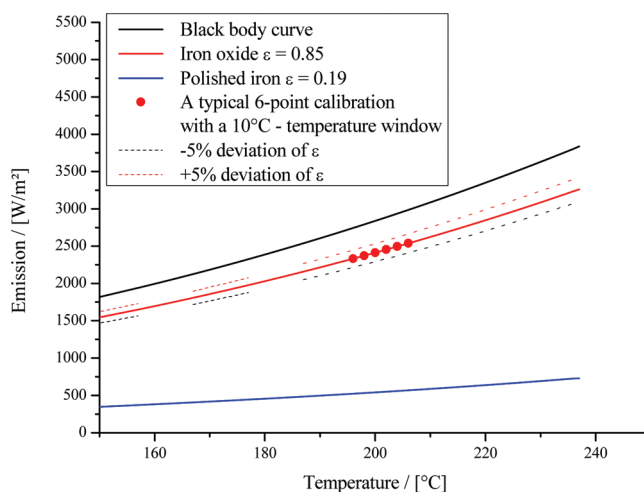
**Figure 2.** ecIRT image of the library from Figure 1 in a reactive atmosphere consisting of 4% methane in air.  $\text{Co}_{70}\text{Mn}_{20}\text{Ni}_{10}\text{O}_x$  is the most active catalyst.

from IR images several factors have to be taken into account. In contrast to visual images of (nonglowing, nonluminescent) objects, infrared images not only consist of reflected radiation but of a mixture of reflections and the IR radiation emitted by the objects themselves. Since regular materials are not ideal black bodies, their IR radiation changes with composition and surface structure (emissivity). Therefore the camera registers different values for different materials at a given temperature. Such gray-body behavior (gray bodies: emissivity  $< 1$ ; reflectivity  $> 0$ ;  $\Sigma = 1$ ) is described by the emissivity  $\epsilon$  which is defined as the quotient of the radiated power and the blackbody irradiance for the given temperature  $E_{\text{real}}/E_{\text{ideal}} < 1$ . The emissivity is not only dependent on the object observed but also wavelength and angle-dependent. The angle-dependence of the emissivity is easily corrected by choosing a static angle of observation (normally  $\sim 180^\circ$ ). The wavelength dependency is neglected using the gray-body assumption.

When detecting large temperature differences the aforementioned effects can be disregarded, but when effects in the area of a few degrees Celsius are to be observed, background correction becomes necessary. Such background correction is usually obtained by subtraction of a frame taken under inert conditions from the frame taken under reaction conditions, which is termed “emissivity-corrected infrared thermography” (ecIRT). It ideally eliminates emissivity differences on the area examined and thus provides exclusively temperature changes, which occur during a reaction. To assign temperatures to image areas, the emissions of each detector pixel at a range of temperatures must be known. This information is obtained by a multiple-temperature calibration. Under inert gas conditions (no reactions may take place) images of the area studied (in our case of a catalyst library) at different temperatures are recorded. Now the camera software is able to identify the temperature of a pixel under reaction conditions by comparing it with the pictures obtained under inert conditions at different temperatures.

To visualize the data a false-color image is computed. Herein different colors are assigned to the temperature changes measured. Despite the elaborate calibration and corrections one should keep in mind that ecIRT is only a screening tool with limitations, since side reactions, absorption effects and changes of the material surface structure may lead to misleading results. For example a partial reduction of a metal oxide catalyst can cause a dramatic emissivity drop ( $\epsilon_{\text{iron rusted}} = 0.85$ ;  $\epsilon_{\text{polished iron}} = 0.04\text{--}0.19$ )<sup>5</sup> which the camera software would identify as a temperature change.

Figure 3 shows the emission of a blackbody radiator in  $\text{W}/\text{m}^2$  in comparison to gray-body emitters and a typical 6-point



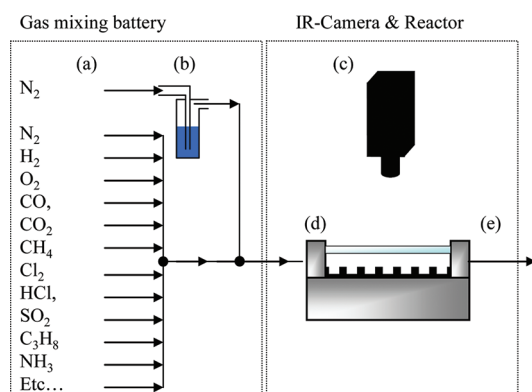
**Figure 3.** Emission of black and gray-body radiators.

calibration window as it is used in our research group. The  $\pm 5\%$  emissivity curves show that even small changes in the surface morphology of the observed object may shift the emissivity curve rendering a prior made calibration invalid.

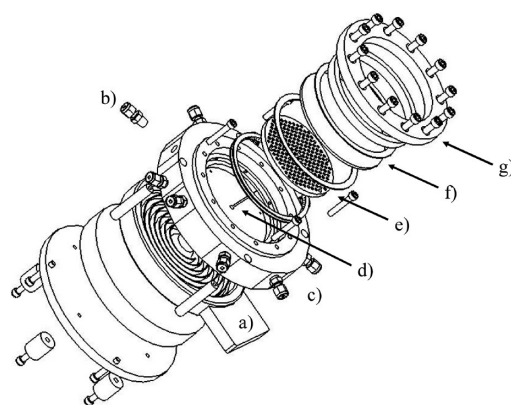
Another, not so obvious problem occurs with libraries containing materials of different microstructures. Different microstructures (porosity and pore size, surface area, particle size) lead to different heat and mass transport phenomena and emissivities, which can as well falsify the ecIRT results.<sup>6</sup> Best results with such combinatorial libraries for material screening by ecIRT are obtained, when all materials on a library behave as similar as possible, this means, with regard to microstructure, that they should have been prepared by the same basic recipe and calcination procedure. It is therefore disadvantageous to collect all kinds of different materials for comparison in such an experiment.

## ■ SETUP

Figures 4 and 5 show a general scheme of the setup as it is used in our research group. The camera is focused with something giving good IR contrast (f.e. a piece of microstructured wafer), which is placed on the sapphire window. In contrast to the catalyst libraries the small structures on the thermoresistant wafer have significantly different emissivities that are clearly visible in the real-time IR image. The software *IRTestRig*<sup>7</sup> is used to control the IR camera, the temperature of the reactors and the tubings, the mass flow controllers and the valves. The cameras used (from Thermosensorik Corp.) are equipped with a PtSi detector. PtSi detectors are photovoltaic detectors with a working range of  $1\text{--}5\ \mu\text{m}$  and a thermal resolution of  $\Delta T \geq 0.05\ ^\circ\text{C}$ . What made them stand out against other IR detection systems, such as MCT (Mercury–Cadmium–Telluride detector) or InSb (Indium–Antimonite detector), was their small baseline drift, guaranteeing that the calibration will be stable over the course of the next hours or even days. It should be noted however, that since then the usability of other detection systems has improved significantly. The reactors used were designed and built in house. The main challenges hereby was the homogeneous distribution of the inflowing gas which was achieved with the help of a radial gas distribution ring and a



**Figure 4.** Schematic drawing of a typical IR reactor setup. Shown are the gas mixing battery for up to eight gases at a time (a), a washing bottle used to add volatile compounds like water, cyclohexene or thiophene to the gas stream (b), the IR camera with PtSi detector (Thermosensorik Corp.) (c) and the Inconel reactor (d) (see Figure 5 for exploded view). The exhaust gas (e) may be subject to further analysis like FTIR or GC/MS.

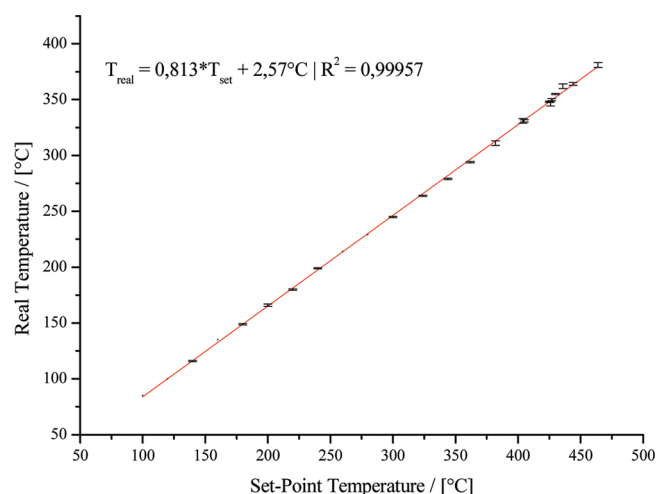


**Figure 5.** Exploded view of the Inconel reactor with heating device (a), one of eight gas inlets (b), reactor (c), cut out for the thermocouple (d), 206 well catalyst library (e), IR transparent sapphire window (f), and seal rings (g).

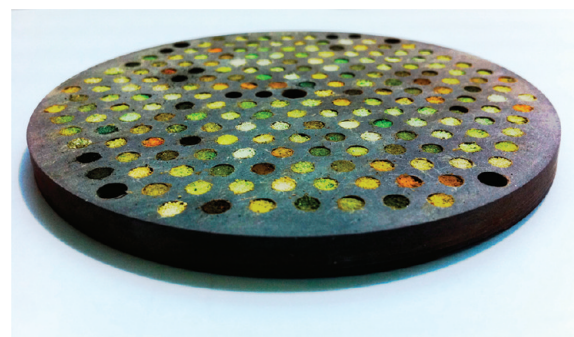
homogeneous nonoscillating temperature profile ( $\Delta T < 1\text{ }^{\circ}\text{C}$  for twelve minutes or the calibration is aborted) which was made possible by the use of a flat heating unit placed directly under the library (see Figure 5) and the use of a carefully insulated reactor with a large heat capacity.<sup>8</sup> The reactor shows a linear correlation between the temperature of the heating unit and the temperature measured in the wells of the library (see Figure 6). Sapphire windows tailor-made from Opto-Sytem-Technik Corp. have been chosen due to their good and even IR transmissivity.

The library plates used in our setup, fabricated by our local machine shops, were made of slate, which was selected due to its inertness, low level of optical noise (reflections, etc.; see also Figure 16) and machinability. A photograph is shown in Figure 7. They contain 206 wells that can be filled with materials. A larger hole at the center serves as the gas outlet. Four symmetric holes are used for handling and accurate positioning of the plates.

The software *Plattenbau*<sup>9</sup> has been used for the planning of the automated synthesis of our catalysts using sol-gel-recipes and pipetting robots for the design of the catalyst libraries and for the generation of the individual synthesis recipes (see Figure 8 and Figure 9). It automatically generates pipetting lists and



**Figure 6.** Linear correlation between the temperature set and the temperature measured in the wells of the slate library. The temperature difference  $\Delta T$  between center and periphery of the slate library is about  $1\text{ }^{\circ}\text{C}$  at  $300\text{ }^{\circ}\text{C}$  and about  $4\text{ }^{\circ}\text{C}$  at  $400\text{ }^{\circ}\text{C}$ .



**Figure 7.** Slate library with a diameter of 10 cm. Each of the 206 wells is filled with about 8 mg of doped CuTi oxides.

sends them to the associated pipetting robots, which are then used to automatically generate the sol-gel reaction mixtures, which turn into the desired catalyst material upon gelation, drying and calcination.

## ■ APPLICATIONS

EcIRT has been used by our research group since 1998.<sup>4</sup> Over the course of the years a diverse range of research projects belonging to the field of heterogeneous catalysis has been worked on. In the first part of this section we will give a short chronological overview about projects in our group. In the second part we will present selected thermography publications from other research groups with a focus on catalysis and HTE.

In 1998, the hydrogenation of 1-hexyne and the oxidation of isooctane have been studied.<sup>4</sup> In the year 2000 monitoring of the time dependent catalyst deactivation during the oxidation of toluene was published (see Figure 10).<sup>10</sup>

In 2003, ecIRT was applied to the oxidative dehydrogenation (ODH) of *n*-butane.<sup>11</sup> In 2004, new catalysts for the oxidation of CO at room temperature were discovered using IR thermography.<sup>12</sup> Three years later a catalyst system for the selective methanation of CO in the presence of CO<sub>2</sub> was developed.<sup>13</sup> In 2008, ecIRT was applied for the "HT Search for Alkaline and Noble-Metal Free Mixed Oxide Catalysts for Soot Oxidation"<sup>14</sup> and the study of topographic effects on catalytic activity.<sup>6</sup> Catalysts synthesized by flame spray pyrolysis

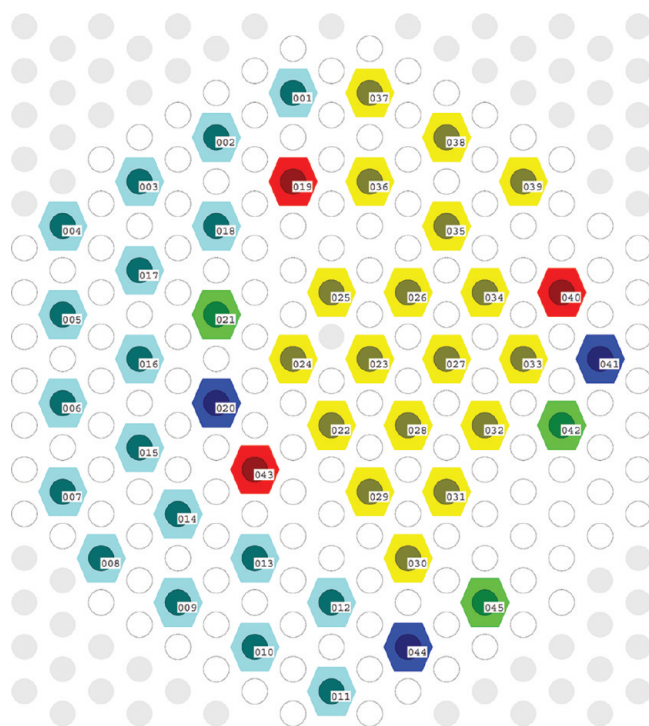


Figure 8. Catalyst library designed and displayed with the software Plattenbau.

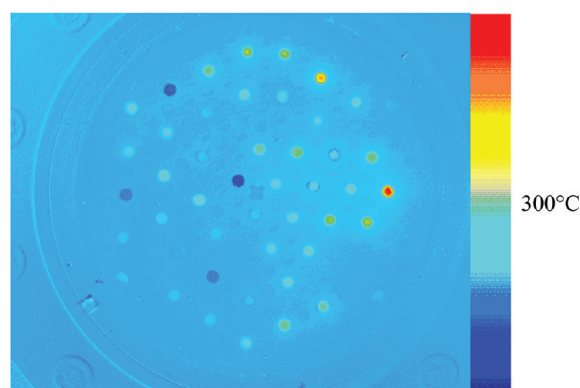


Figure 9. Library shown in Figure 8 in use for the oxidation of carbon monoxide.

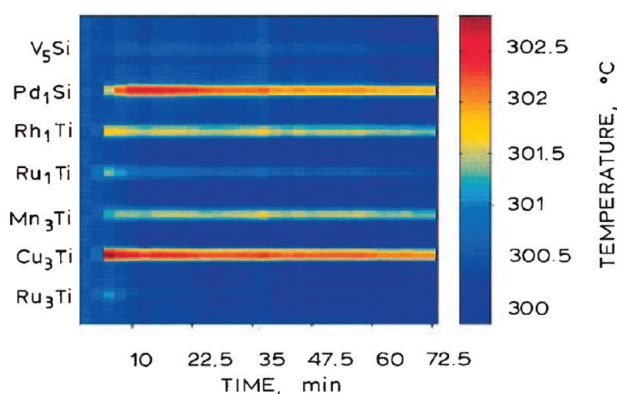


Figure 10. Time-dependent catalyst deactivation during the oxidation of toluene in air.<sup>10</sup>

have been investigated for their activity for hydrocarbon/ $\text{NO}_x$ -oxidation in 2009.<sup>15</sup> Recent eCIRT projects deal with hydrogenations<sup>16,17</sup> and hydrodesulfurization,  $\text{SO}_2$  oxidation,<sup>18</sup> the oxidation of waste gases in the presence of methyl bromide<sup>19</sup> and the Deacon process. eCIRT has become part of the bachelor of chemistry education at the University of Saarland and is mediated in lectures and laboratory exercises.

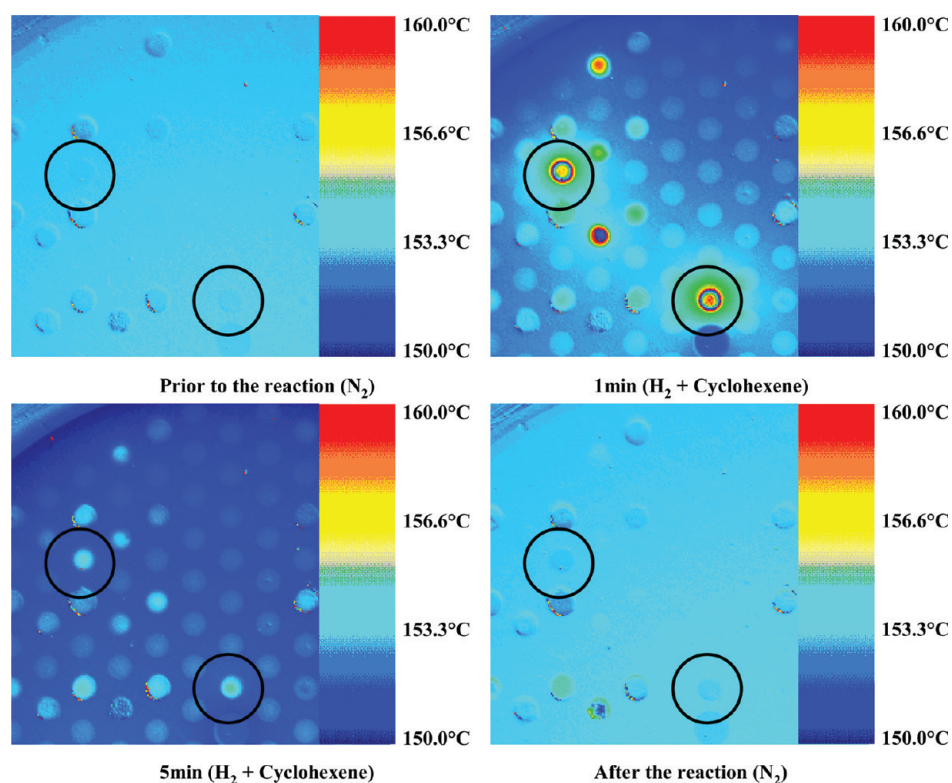
Other groups have used IRT in catalysis for a wide variety of applications. In this part of the review a number of selected publications are highlighted. The publications were selected due to the unconventional problem solution presented or due to the general impact of the research on IRT in catalysis.

In the examples presented either multiple catalysts were investigated in parallel or IRT was used as a calorimetric tool to gather specific information on a catalytic process.

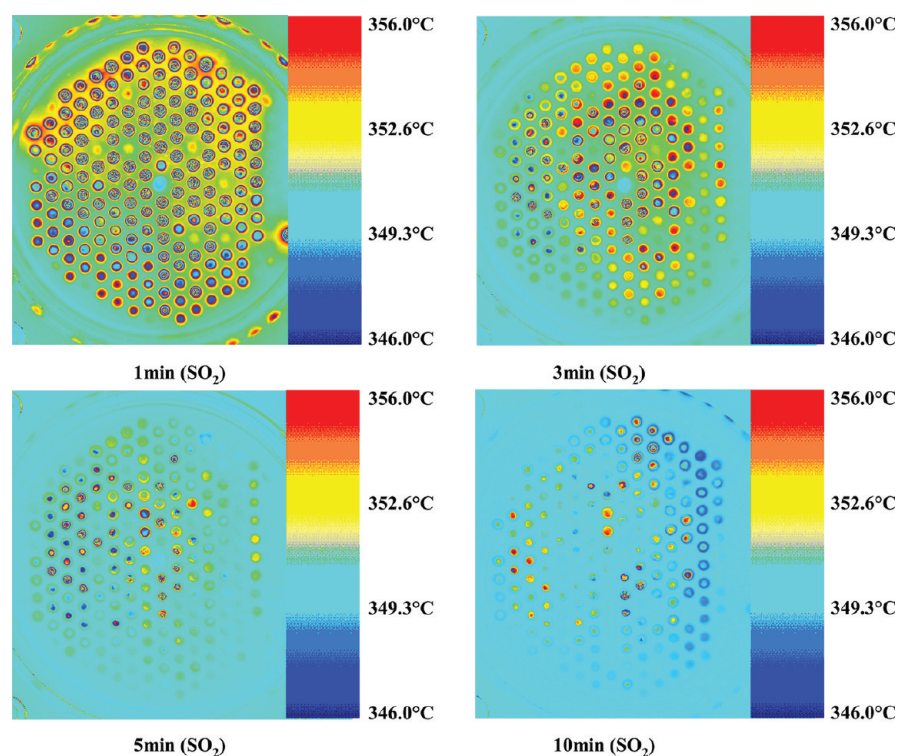
Such a calorimetric investigation is the determination of the concentration of absorbed nitrogen oxides with time and space resolution on Pt/Ba/ $\text{Al}_2\text{O}_3$  storage/reduction catalysts. To estimate the concentration Epling et al. used an indirect method and observed the exothermic reduction of the nitrogen oxides during the regeneration cycle.<sup>20</sup> Another good example to show the versatility of IRT as a contactless calorimetric tool is its application in dental medicine. In 2008 the method was applied to investigate the in vitro raise of temperature in human teeth when a bleaching paste containing peroxides and catalyst applied to the teethes is irradiated by either halogen light or a diode laser.<sup>21</sup> Thermal oscillations of individual catalysts were also subject of detailed investigations. Orlik et al. have shown that IR images together with images of the optical patterns of the oscillating catalytic Belousov–Zhabotinsky reaction give valuable extra insight into the thermal driving forces of this complex reaction,<sup>22</sup> while Grunwaldt et al. investigated the oscillating behavior of the temperature on a solid oxide Pd/ $\text{Al}_2\text{O}_3$  catalyst during the partial oxidation of methane.<sup>23</sup> The group of Wolf et al. used IRT for observation of individual catalyst behavior<sup>24–26</sup> as well as for HT studies, such as the screening of catalysts for the preferential oxidation of CO or the hydrogen production from methanol.<sup>27,28</sup>

Several other groups conducted HT studies with setups comparable to those used by us. Symyx Technologies used a HT-IRT system to monitor the oxidation of CO and volatile organic compounds at low temperatures.<sup>29–31</sup> Sairyó et al. used such a setup to investigate effects of preparation method and catalyst loading on the activity of carbon nanotube supported platinum catalysts for the combustion of hydrogen.<sup>32</sup>

IRT is not limited to studies of heterogeneous solid/gaseous systems. Even reactions at liquid/solid interfaces or homogeneous reactions in the liquid phase have been observed. In 1998, Morken et al. used IRT to identify hot beads created by split and pool techniques for acylation reactions. Therefore a tagged library of 3150 distinct catalysts on beads was designed. The beads were freely floating in a solution of chloroform containing the reactants. Chloroform being denser than the beads guaranteed that they float on top and remained thus visible for the camera. With the help of the IR images the promising candidates were picked and the catalyst compositions were identified by the tags on the beads.<sup>33,34</sup> In 2001 Fuerstner et al. used IRT to develop new second generation ruthenium based N-heterocyclic carbene ligand metathesis catalysts for the ring closing alkene metathesis and the intramolecular enyne cycloisomerization reaction in the liquid phase.<sup>35</sup> In another example of IRT use applied to homogeneous solutions Berkessel et al. monitored the rare



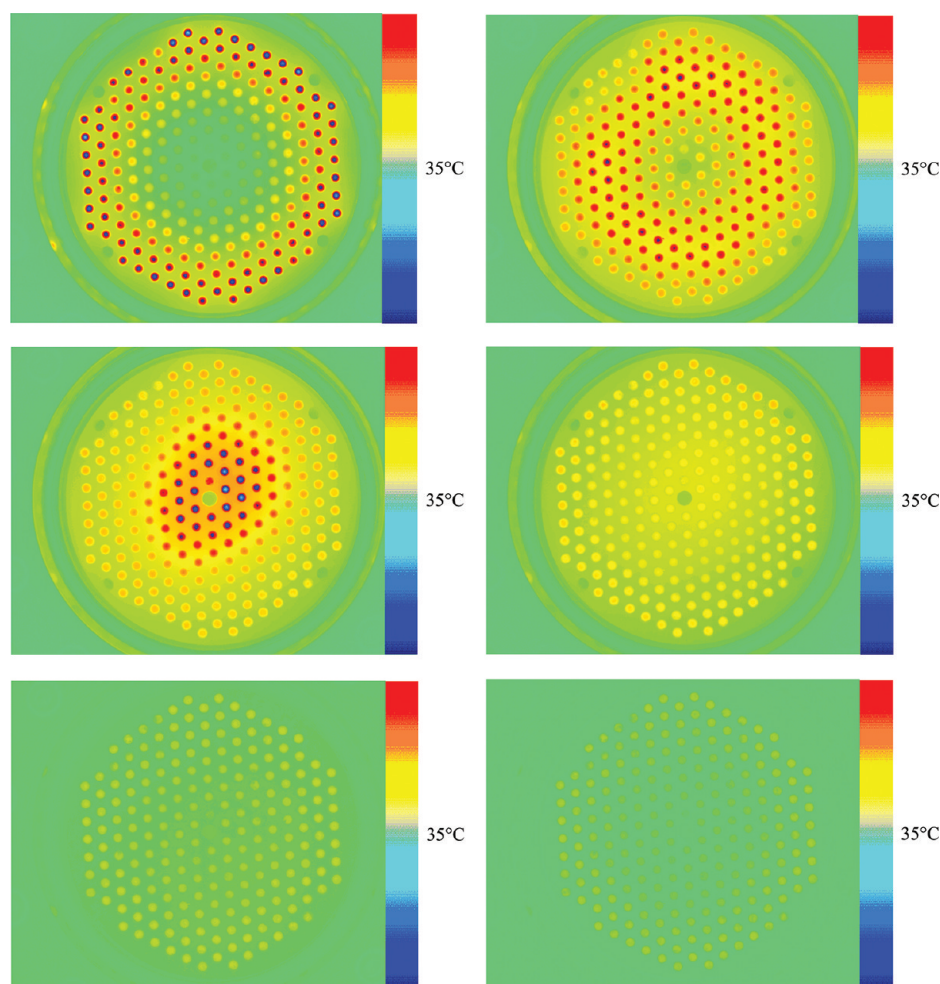
**Figure 11.** Heat of hydrogen and cyclohexane absorption on a metal sulfide containing catalyst library. Pretreatment of the catalyst library in  $\text{H}_2$  at 200 °C. Background image and temperature calibration in  $\text{N}_2$  atmosphere. Black circles mark overshooting catalysts.



**Figure 12.** Heat of absorption of  $\text{SO}_2$  on Fe–Mo oxide catalysts.

earth triflate catalyzed ring-opening of epoxides and the Baeyer–Villiger oxidation of cyclobutanones with hydrogen peroxide in dichloromethane solution. Scandium(III), that was never before reported as a catalyst for this reaction, was found to have outstanding activity.<sup>36</sup>

With the help of IRT, phase transitions could be studied during the cationic ring-opening polymerization of multiple batches of 3-ethyl-3-phenoxy-methyloxetane.<sup>37</sup> Even enantioselective catalysis has been investigated using IRT. Reetz et al. reported in 1998 the use of eCIRT for time-resolved screening



**Figure 13.** From top left to bottom right the heat of absorption of ammonia on a reference library of identical porous materials (zeolite mordenite) at 35 °C after 1, 1.5, 2, 3, 5, and 15 min under a gas stream of  $N_2/NH_3$ .

of enantioselective reactions in liquid phase.<sup>38</sup> In 2002, the parallel screening for the enantioselective substrate specificity of candida antarctica lipase in the liquid phase was reported.<sup>39</sup> The heat generated over an enzyme was shown to linearly correlate with the *ee* value.<sup>40</sup>

#### ■ TYPICAL PROBLEMS LEADING TO MISINTERPRETATION OF IRT DATA

The last section covers reoccurring phenomena of eIRT, which the observant, if not careful, may misinterpret as too high or too low activity of the materials. The effects can be classified in absorption effects, side reactions, reflections, high temperature effects, shadow effects, and emissivity changes.

**Absorption Effects.** Upon injection of the reaction gases a steep temperature increase may occur, followed by a rapid temperature decrease. Such effects are shown in Figures 11–13. They can be differentiated from irreversible effects, such as rapid catalyst deactivation and can be identified as absorption effects by their reproducibility.

A phenomenon common in eIRT experiments is the overshoot of local temperature above the calibration range, indicated by a more than complete cycle through the colors of the calibration cycle. In Figure 11, upper right image, this is occurring at the catalysts marked by the black circles. The catalysts temperature increases already at the rim of the catalyst

wells to over 160 °C and reaches about 164 °C in the upper and 168 °C in the lower marked position.

Figure 11 shows the heat of absorption of  $H_2$  and cyclohexene. After switching on the cyclohexene and  $H_2$  gas streams the catalysts marked by circles show a strong temperature increase far above 160 °C, as indicated by the color bar. After five minutes the effect has abated and catalyst temperature remains stable for the rest of the catalytic run (1 h) indicating a stable catalytic performance. The image taken after the reaction confirmed that nearly no emissivity change occurred.

The heat of absorption of  $SO_2$  shown in Figure 12 exceeds the preset calibration window of  $\Delta T \leq +6$  °C. Therefore at the start of the reaction, the camera software cannot assign temperatures to the individual pixels (noisy signal). Plug flow reactor tests with a thermocouple placed inside a packed bed of 100 mg catalyst mixed with 100 mg of sand confirmed temperature increases of 30 °C and more upon initial contact of the catalysts with  $SO_2$ .

In Figure 13 the absorption of  $NH_3$  near room temperature on a library filled with the identical highly porous zeolite mordenite in all wells is shown. The six images from upper left to bottom right show an absorption, which is so intense, that the gas flowing from the inlets on the outer reactor wall to the outlet at the center of the library is completely depleted of  $NH_3$  (see also under shadow effect). Therefore the catalysts in the

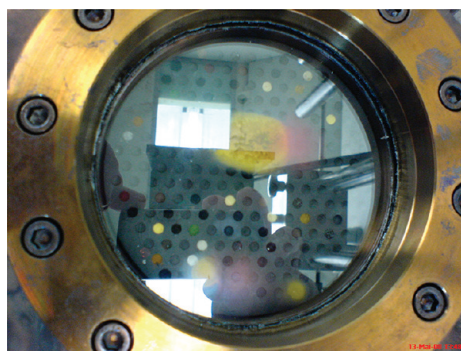
middle can only start to absorb when the outer catalysts are already ammonia-saturated.<sup>41</sup>

**Side Reactions.** Two main types of side reactions may occur during a gas phase experiment. The first one being that multiple reactions may take place.

In a complex gas mixture such as exhaust gas containing  $\text{NO}_x$ ,  $\text{CO}_x$ , hydrocarbons,  $\text{N}_2$  and  $\text{O}_2$  the camera only sees the total temperature increase due to all reactions at a time: NO oxidation to  $\text{NO}_2$ , NO reduction to  $\text{N}_2$  or the dominance of one of these two reaction paths depending on gas composition, CO oxidation and hydrocarbon oxidation. With the help of multiple experiments (for example in different atmospheres) and an elaborate calibration, evidence for the selectivity of the catalysts can be extracted from the data. It is possible, for example, to use images of a library in hydrocarbon-containing air as a background image for a measurement in a mixture of air, hydrocarbons and CO to highlight the effect of CO in such a system.<sup>42</sup> In general, care has to be taken, in which atmosphere the background correction image is recorded. It can make a huge difference, if the background correction is recorded in the absence or presence of  $\text{O}_2$  in  $\text{N}_2$ , or simply in  $\text{N}_2$  or in Ar. In the development of experimental conditions for such a high-throughput experiment, it is essential to properly select suitable conditions for background correction. The problem has been addressed in a search for new selective catalysts for hydrocarbon oxidation.<sup>43</sup>

Some reactants may also allow for multiple reaction products during a reaction sequence. This occurs when partial and total oxidations can take place as well as in cases where hydrogenations and dehydrogenations are catalyzed. For example during the hydrogenation of cyclohexene at higher temperatures not only cyclohexane but also 1,3 and 1,4-cyclohexadiene and benzene were identified via GC-FID analysis.<sup>17</sup>

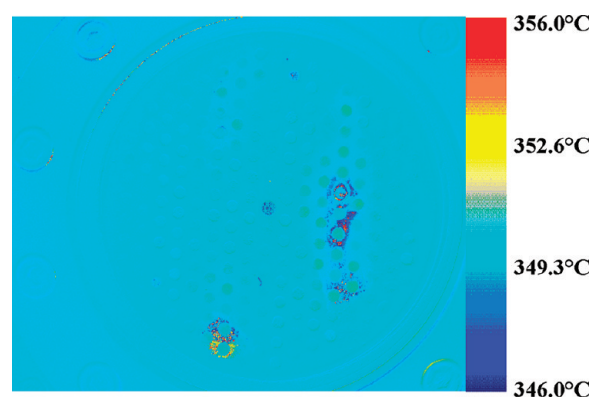
Another type of side reactions involves changes of the catalysts or materials by reaction with one of the reactants. Figure 14 shows deposits of sulfur that condensed on the inside



**Figure 14.** Deposition of sulfur on the sapphire disk which is slightly colder than the catalyst library formed during a hydrogenation reaction catalyzed by transition metal sulfide catalysts.

of the sapphire window during a search for new hydrogenation catalysts based on mixed metal sulfides. In Figure 15 some catalysts decomposed forming a layer of ceria on parts of the sapphire disk above. This white  $\text{CeO}_2$  layer is partially IR transparent casting a “shadow” on the catalysts below.

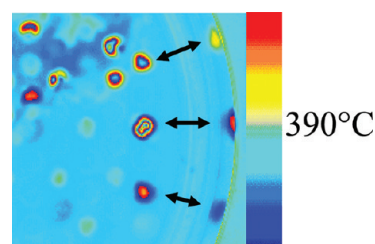
Another example for side reactions are copper-based catalysts, whose potential for the oxidation of  $\text{SO}_2$  was investigated. At first they showed promising IR activity but



**Figure 15.** IR image of a library containing mixed oxide catalysts for the oxidation of  $\text{SO}_2$  in air (no reaction) with deposits of ceria on the sapphire window casting a “shadow” on the spots below. The IR radiation can penetrate these layers up to a certain extend.

tests in a plug flow reactor revealed, that while the materials were able to take up vast amounts of  $\text{SO}_2$  in an exothermic reaction, only trace amounts of  $\text{SO}_3$  were produced. XRF experiments confirmed that sulfatization of the materials, resulting in emissivity and temperature changes, were responsible for the temperature raise.<sup>18</sup>

**Reflections.** Materials of high reflectivity, such as steel, can reflect IR radiation, which is detected by the camera. Figure 16



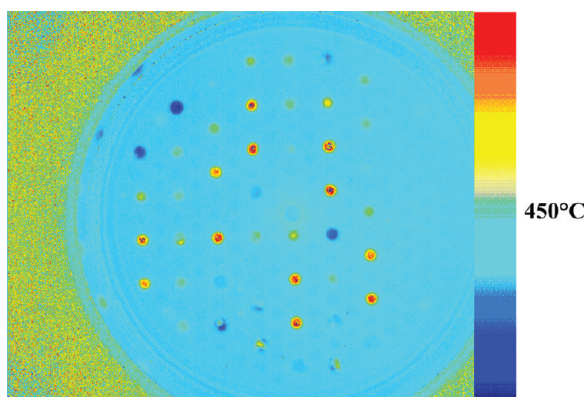
**Figure 16.** Reflection of IR radiation by the walls of the reactor.

shows an IR image with the reflections of three active catalysts on the Inconel wall of the reactor (marked by arrows). To avoid such confusing phenomena, nonreflective library materials, such as slate or oxidized metals should be chosen for IRT studies.

**High-Temperature Effects.** At high temperatures two main factors have to be considered. The emission of the IR reactor is so high that even at the shortest integration time the IR sensors are overexposed. Here three germanium based neutral density filters (Thermosensorik) which filter wavelength independent in the range of 2–20  $\mu\text{m}$ , have been used. They transmit only 10%, 1%, or 0.1% of the emitted radiation and are placed in the lens system of the IR camera.

The second problem is caused by the high energy loss of the reactor. The higher the temperature the more likely are temperature oscillations of the reactor and the higher is the temperature gradient. To address this, the reactor has been packed in additional isolating rock wool layers and prior to every IR image the reactor has to be returned to the desired temperature.

An image grabbed at 450 °C can be seen in Figure 17. The temperature at the outer part of the reactor is not homogeneous due to the insulating rock-wool having a temperature significantly below the calibration window. For

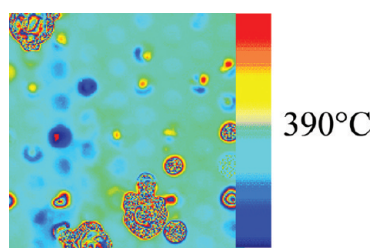


**Figure 17.** EcIRT image of a material library containing vanadium based materials for the oxidation of  $\text{SO}_2$  under high temperature conditions. The image was grabbed by using a germanium based filter system (1% transmission).

comparison see Figure 9, where even details such as screws are visible in the outer parts of the IR image.

**Shadow Effects.** These effects occur when either the gas distribution on the surface of the library is inhomogeneous or when the outer catalysts of the library are active enough to convert a significant amount of the inflowing reactants. In either case the result is that the reactant concentration becomes a function of the position and therefore misleading conclusions based on the IR emissions may be drawn. To detect such shadow effects each catalyst sample is positioned more than once on the library. An image with severe shadow effects can be seen in Figure 13 (upper left). To extract data from libraries that show a shadow effect, one has to either increase the gas flow rate or to inverse the direction of the gas flow (from center to outer ring) to study the activity of the catalysts placed at the center or to lower the temperature to reduce the overall activity of the library. If that is not sufficient, a new library containing less catalyst material, for example by diluting the catalysts with inert material, has to be made.

**Emissivity Changes.** Emissivity changes occur, when the surface of the material significantly changes under reaction conditions, for example due to a solid gas reaction on the catalyst surface. When the emissivity change is small, it can be overcompensated by the heat of the reaction. If large, it can lead to false negative or false positive results, for example when the heat of the reaction is negated by the emissivity change. If the emissivity change is too large the camera software is unable to assign temperatures to the areas of interest. Figure 18 displays an IR image of a library showing emissivity changes. Some of the spots appear to be colder than the reactor, others show apparent random temperature fluctuations indicative of



**Figure 18.** IR images of a library containing supported molten salt catalysts showing different types of emissivity changes.

temperatures significantly out of range of the calibration window.

To handle emissivity changes several strategies can be used. First, one can try to make additional measurements with the library. If the change of the catalyst surface is permanent and completed, a second calibration may record new and stable emissivity values. Another method is the use of background images for the emissivity correction taken after the measurement instead of prior to the reaction. These background images made under inert gas conditions subsequent to the measurement contain the permanent emissivity changes without the heat of the reaction. With this method small errors can be easily adjusted.

## SUMMARY

IR thermography has been developed into a versatile and powerful tool for rapid and parallel screening of catalyst and materials properties associated with temperature changes. Impressive sensitivities even over long time experiments can be obtained by the use of emissivity-corrected IRT (ecIRT). Nevertheless, application of IRT is not trivial and, as outlined, the user has to be aware of many potential sources of error, such as changes of emissivity due to various causes, observed temperature exceeding calibration range, undesired reflections, shadow effects, sublimations and absorptions. The biggest drawback of IRT, especially for its use in high-throughput experimentation, is the lack of suitable commercial software, which combines camera control, background correction and temperature calibration with image processing (f.e. spot recognition and integration) and data extraction.

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### Notes

The authors declare no competing financial interest.

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