Catalytic Phenomena in Combinatorial Libraries of Heterogeneous Catalysts

DETECTION OF ACTIVATION AND DEACTIVATION BY EMISSIVITY-CORRECTED IR THERMOGRAPHY

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Combinatorial catalysis is becoming a significant method for investigating the activities of large numbers of potential catalysts. A very important prerequisite for making use of combinatorial catalysis research is a reliable, fast and efficient technique for monitoring the catalytic activities. Emissivity-corrected infrared thermography, which monitors the heat changes resulting from the heat of reaction on catalyst surfaces, is such a technique. In this article we describe emissivity-corrected infrared thermography and demonstrate its performance, over time, in monitoring the catalytic activities of catalyst libraries. It is shown that not only can static relative activity be displayed, but also that catalyst-specific time-dependent properties, such as activation and deactivation phenomena can be demonstrated.

The successful application of combinatorial screening techniques as powerful research tools in the pharmaceutical industry (1) has tempted researchers to extend this approach to other fields of science. The application of screening techniques to materials science seems especially well suited since in many cases improvements to existing materials can only be made by employing complex mixtures of components (2). The increased number of parameters resulting from such multi-component mixtures makes it impossible to screen the whole parameter space by applying traditional one-by-one test procedures.

Improvements in catalytic materials for bulk chemical processing can result directly in large-scale cost savings – due to their immense economic importance. However, as far as heterogeneous catalysts for gas-phase reactions are concerned, few reports have appeared in the literature on the application of combinatorial screening techniques. These techniques detect the reaction products by mass spectrometry (3), by resonance enhanced multiphoton ionisation (REMPI) (4) and by the IR thermographic detection (5, 6) of the catalytic activity by associated heat changes. REMPI should allow parallel monitoring of the amount of one product formed during a catalytic reaction, but it is limited to reaction products such as benzene for which selective ionisation in sufficient yield can be achieved – at a certain wavelength of laser light. IR thermographic methods, while not able to resolve product compositions, have the advantage of higher throughput as well as greater simplicity and flexibility, so they are not limited to gas-phase reactions and can also be applied to liquid-phase (7, 8) and polymerisation reactions. In contrast to mass spectrometric techniques, which involve sequential testing of each catalyst spot, IR thermography is an intrinsically parallel screening technique. All of the catalyst spots on the library can be imaged at the same time under identical reaction conditions. The technique is therefore very well suited for high throughput screening of large libraries.

By contrast, screening methods which employ sequential testing may be time-consuming and the time lag between testing different catalyst spots may become considerable for a large library. If the whole catalyst library is maintained at high reaction temperatures and heat induced catalyst deactivation phenomena occur, then under sequential operation the catalyst spots are not tested under identical conditions. With IR thermographic detection the time evolution of catalytic activity occurs simultaneously for all catalysts on the library. If sequential mass spectrometric screening techniques

were used, the same experiment would be more time consuming.

For practical applications, catalysts which have constant activity are obviously more desirable than catalysts having high initial activity and fast deactivation, and therefore information about the time evolution of catalytic activity is very useful. As will be shown here, such deactivation phenomena are readily detected with video IR thermographic methods.

Corrections Required for IR Thermography

Before IR thermographic methods can be applied successfully to screen heterogeneous catalyst libraries in gas-phase reactions, a few problems have to be addressed. First of all, the different catalyst materials on the library may emit different amounts of IR radiation even if their surface temperatures are identical. Such emissivity differences can be misinterpreted as temperature differences, and therefore have to be corrected. To be able to image the temperature changes in real time during a catalytic experiment, suitable calibration data which account for these emissivity differences have to be recorded prior to the experiment.

Below we describe the technique of emissivity-corrected IR thermography (ECIRT) as it is applied in our laboratory and give an example where time resolved monitoring of catalytic activity on a model combinatorial library is demonstrated. A schematic drawing of the IR-camera with a PtSi-Focal Plane Array (FPA) detector can be seen in Figure 1 (9). The main component of the camera is the detector with 256 × 256 detector elements on a FPA-chip which is sensitive to radiation in the range of 3 to 5 μm. The detector is cooled to liquid nitrogen temperature by a Stirling heat exchanger. Analog data from the camera are digitised in the analog/digital converter and correction to the detector response is performed in real time in a Digital Signal Processing (DSP) unit which also reduces the IR data from a 14-bit to an 8-bit format. In the framegrabber, colours are assigned to the 8-bit values from the DSP so that the data can be visualised on a colour monitor.

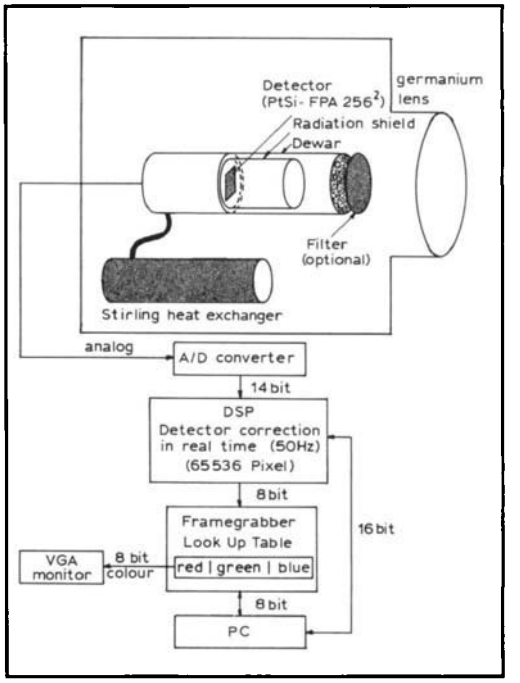
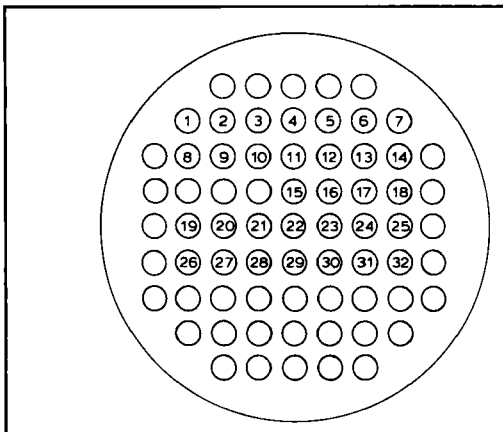


Fig. 1 Schematic drawing of the AEGAIS-IR camera from AIM (AEG Infrared Module) with a 256 × 256 PtSi-FPA detector

A common problem of all high resolution FPA-IR cameras is the inhomogeneity of the detector response (10, 11). It is not possible to fabricate the detector elements with sufficient precision so that all detector elements have the same response to IR radiation. To reach sufficient temperature resolution the differences of the individual pixels of the detector have to be electronically corrected. This task is performed by the DSP unit in real time on the basis of correction data which have to be calculated from calibration images taken with the camera prior to the experiment. The PtSi-FPA detector used in our experiments shows a very stable response with time so that the calibration data retain their validity for more than 24 hours. In the case of other commonly used FPA-detector materials, which employ the compound semiconductors indium antimonide and cadmium mercury telluride, the detector response is not stable with time so that frequent recalibration of the detector is necessary. The advantage of compound semiconductor FPA detectors is their higher sensitivity to IR radiation. High sensitivity is an advantage if fast



1 V_5SI
2 Pd_1Si
3 Rh_1Ti
4 Ru_1Ti
5 Mn_3Ti
6 Cu_3Ti
7 Ru_3Ti
8 Ag_2Ti
9 Zn_3Ti
10 Ir_3Ti
11 Cr_3Ti
12 Ni_3Ti
13 Co_3Ti
14 Rh_2Ti
15 $In_{10}Si$
16 Re_2Si
17 Cu_6Si
18 Ta_2Si
19 Cr_2Si
20 Sb_2Si
21 Ru_2Si
22 Ir_2Si
23 Ni_2Si
24 Rh_2Si
25 Os_2Si
26 V_2Si
27 Sn_3Si
28 Au_2Si
29 Te_2Si
30 Mo_2Si
31 Mn_2Si
32 Co_2Si

Fig. 2 The configuration of the catalyst library: the composition of the binary oxide catalysts on the library according to the AMM notation (the molar percentages of active metal oxide and base metal oxide are given, such that AMM-V_5Si stands for 5 mol% vanadium oxide in 95 mol% silicon dioxide)

moving objects have to be imaged as high frame rates can then be applied. It may also be useful for imaging objects at low temperatures, such as room temperature or below. At the elevated temperatures used in our experiments, the amount of emitted IR radiation is quite high, so enough photons are available for detection. Also, as no moving objects are observed, signal averaging can be employed to improve the signal to noise ratio further. In fact, the higher sensitivity of the compound semiconductor detectors is not needed for our experiments.

The correction algorithm used in the camera is based on work by Schulz and Caldwell (11). Basically, calibration images of the library have to be taken at three different temperatures from which a linear correction (gain correction) and an offset correction (image subtraction) are calculated. The image for the offset correction is ideally taken at the final reaction temperature – just before the start of the catalytic experiments. The data are loaded into the DSP unit which then performs the correction in real time. The effect of the correction is that the response of each individual pixel in the detector becomes the same as the average response over the whole detector. Any differences in emissivity on the library surface as well as any temperature differences will be evened out. For imaging of the catalyst library, this means that when no temperature differences occur on the library due to catalytic activity then a structureless image will be recorded. Temperature differences due to catalytic activity can then be easily recognised. Afterwards a temperature calibration can be performed which assigns temperature values to the different colours of the corrected images. Image correction (offset and gain correction) and temperature calibration together make a correction to the emissivity of each spot on the library surface, which allows the photon intensities to be detected as temperature values by the IR camera. Our approach has the advantage that the emissivity correction can be performed in real time by the DSP unit. Other approaches, such as using the Planck formula, require extensive computation and can therefore not be performed in real time. It is essential to have as little differences in temperature as possible on the library since otherwise the correction may become inaccurate.

It is also of general importance to avoid the IR radiation being reflected, especially on the library surface since this can cause artifacts unrelated to catalyst temperature. The IR thermographic method works accurately only if the intensity of emitted IR radiation from each spot on the library surface can be detected, so that the surface temperature values can be calculated and assigned to the location from which the IR radiation was originally emitted. If the emitted radiation is reflected, then the detected information about the location

of the emission is obviously not accurate. Thus, it is very important to select a support material for the library which has low reflectivity for IR radiation.

We have tested different library support materials, such as metals, graphite, slate and others that are stable at high temperatures of a few hundred degrees Celsius and are stable against the strongly acidic solutions of the sol-gel catalyst preparations (6). Supports which have high electrical conductivity, such as metals, can only be used with an antireflective coating, since their surfaces show very high reflectivity for IR radiation. Certain roughened graphite surfaces did show lower IR reflectivity than metal surfaces but were too porous and therefore not impervious to liquids. Slate was finally chosen as the library material because of its low IR reflectivity.

The application of ECIRT to follow catalytic reactions in a time resolved mode has already been demonstrated for liquid-phase reactions (8). The use of this method for the detection of catalytic activity in libraries of heterogeneous catalysts is described below. For this purpose a catalyst library containing amorphous microporous catalyst samples of powdered mixed oxides was prepared by filling each hole of a slate library plate with ~ 1 mg of different catalyst samples. The catalysts were prepared by a sol-gel process (6, 12, 13). This procedure allows the production of a microporous oxide which contains isolated catalytically active centres dispersed in the matrix material. Due to the amorphous nature of the mixed oxide powders there are a few restrictions on the type of elements that can be built into the oxide matrix (12). Most elements of the Periodic Table can be dispersed in different oxide frameworks and thus become accessible as potential catalytic reaction centres. Because of the large number of possible combinations of framework oxide and catalytically active centres, combinatorial approaches are ideally employed for the selection of active catalysts.

The reactor was equipped with an IR-transparent BaF_2 window to allow imaging of the library, and the gas-phase oxidation of toluene with air was chosen as a test reaction (6). Figure 2 shows the chemical composition of the library. All catalysts are binary mixed oxides, for example, oxides of palladium, rhodium, ruthenium, iridium, osmium, gold, silver, copper, zinc, nickel, vanadium, cobalt, tantalum and others, dispersed in a matrix of either titania or silica.

The catalysts on the library were activated by heating at 400°C in a stream of synthetic air for 1 hour to remove any organic residues remaining from their sol-gel preparation. The reactor temperature was then lowered to 300°C and the reaction was started with a constant flow of air and toluene (air:toluene = 25:1) at 20.8 ml min^{-1}. IR images were taken every 2.5 minutes for a total time of 72.5 minutes. Figure 3 shows IR images of the library for different times after toluene was injected into the gas stream.

Active catalysts were found in the first, second and fourth row of the library. Plots showing the time dependency of the temperature profiles along these rows can be seen in Figure 4. In the first row Pd_1Si and Cu_3Ti are very active catalysts: while Cu_3Ti reaches constant activity quite quickly, Pd_1Si needs more time to reach maximum activity and shows slight deactivation. Rh_1Ti and Mn_3Ti show lower but constant activity. Ru_1Ti and Ru_3Ti show

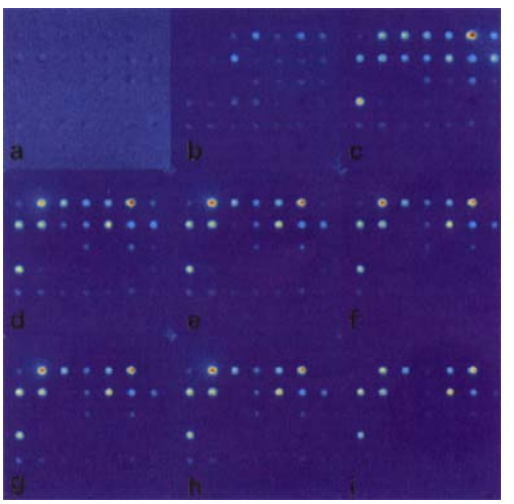


Fig. 3 Emissivity corrected IR images of the catalyst library during the gas phase oxidation of toluene with air at 300°C, before and at different times after the start of the reaction

(a) before *(b) 0 min* *(c) 2.5 min*
(d) 5 min *(e) 7.5 min* *(f) 10 min*
(g) 12.5 min *(h) 15 min* *(i) 72.5 min*

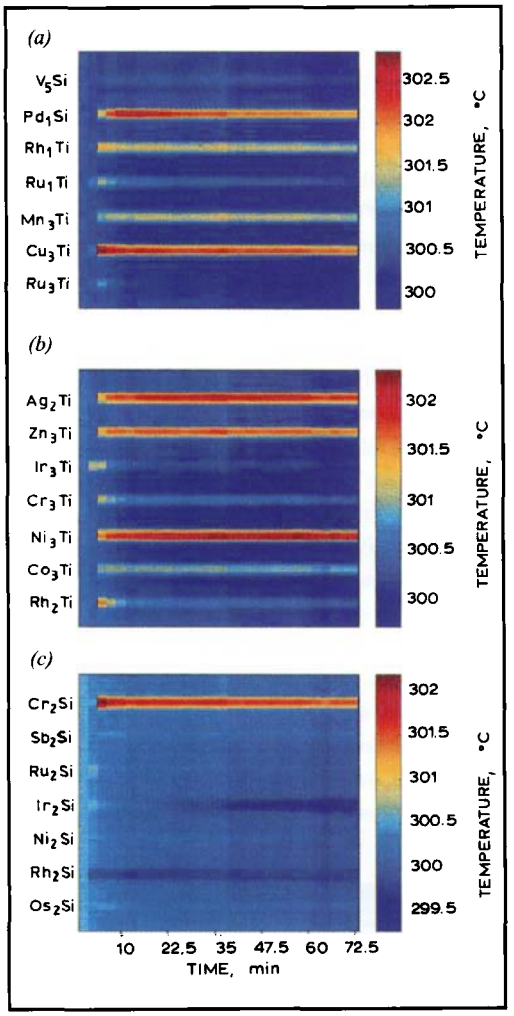


Fig. 4 Temperature versus time cross-sections of the IR images through the catalyst spots on the library. Red colour indicates higher temperature, blue colour indicates lower temperature
(a) first row
(b) second row
(c) fourth row

some initial activity but fast deactivation. In the second row Ag_2Ti, Zn_3Ti and Ni_3Ti are quite active with constant heat response, while Ir_3Ti, Cr_3Ti and Rh_2Ti again show some initial activity but fast deactivation. In the fourth row Cr_2Si shows high activity. In the same row Ir_2Si and Rh_2Si show very small temperature decreases which indicate an endothermic reaction but it is not clear if these effects are real.

Temperature plots of Pd_1Si and Ru_1Ti can be seen in Figure 5; clearly Ru_1Ti shows some initial activity but seems to deactivate quickly. Pd_1Si shows high activity after a period of activation which takes about 10 minutes. Its activity decreases slightly during the course of the experiment.

These observed time dependent phenomena indicate that deactivation (probably due to coking or catalyst changes) occurs. However, it has to be kept in mind that extensive coking or changes in the microstructure of the catalysts may lead to changes in emissivity of the catalyst spots and may give rise to erratic temperature readings. It is more likely that this leads to emissivity increases than to emissivity decreases. To avoid misinterpretations, it is recommended that at the end of an experiment, the reactant gases should be replaced by inert gases, which will allow the immediate identification of catalyst spots where the emissivity has changed during the experiment.

A more detailed investigation of these effects can be performed later with selected catalysts using other techniques, such as mass spectrometry, to detect the reaction products.

Conclusions

Emissivity-corrected infrared thermography allows time dependent phenomena to be observed during a catalytic experiment and is thus useful as a high throughput screening technique. It would ideally be employed at an early stage of the discovery process to narrow down the number of

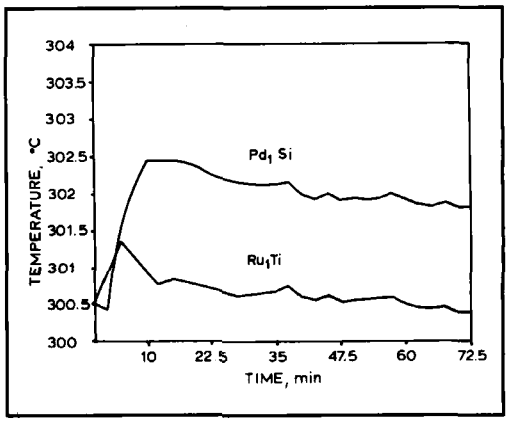


Fig. 5 Temperature versus time line plots through the centre of the catalyst spots Pd_1Si and Ru_1Ti

candidate catalysts. Other combinatorial or even conventional techniques, which give more detailed or complementary information about the catalytic processes involved, could be then employed to aid catalyst selection. Some of these techniques, such as kinetic studies or mass spectrometric screening, are more time consuming due to the much more detailed information obtained; but as a result of employing the ECIRT screening, there are fewer selected candidate catalysts to examine. ECIRT could therefore be applied to reduce the amount of time and effort involved in new heterogeneous catalyst selection for gas-phase reactions.

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Novel Hydrodynamic Ultramicroelectrodes

Ultramicroelectrodes (UMEs) have had great impact on electrochemistry. A novel hydrodynamic UME has now been introduced where mass transfer to the electrode is significantly enhanced by the convective flow of a solution (1, 2). In the microjet electrode (MJE) (1), a jet of solution is fired at ~ 100 m s^{-1} from a nozzle (diameter ~ 25–100 μm) onto a disc UME, typically Pt (diameter 25 μm). The MJE has well defined, variable and high mass transfer rates.

In the radial flow microring electrode (RFMRE) (2), solution flows from a nozzle, placed close to a planar substrate. A Pt ring UME (thickness ~ 100–500 nm) is positioned around the capillary edge, followed by an epoxy resin layer, so only a ring of metal at the capillary end is exposed to solution. The Pt is applied as a paint. As fluid leaves the capillary, it is forced into the nozzle/substrate gap (~ 5–40 μm) and flows radially past the ring electrode. At moderately low volume flow rates, the device has produced the highest steady-state mass transfer rate of any hydrodynamic technique (~ 2 cm s^{-1}).

The high mass transport rates of the MJE and RFMRE have resulted in kinetic applications and possible uses in electrochemical flow systems. When coupled with hydrodynamic modulation voltammetry (HMV) higher detection limits and electrode stability in flow systems can be obtained (1b, 2b).

The MJE-HMV offers the lowest concentration detection limits in a flow system of any hydrodynamically-modulated technique. The mass transport rate is modulated by oscillating the jet to hit and miss the electrode surface. The technique can discriminate against background processes, and $IrCl_6^{3-}$ at 5×10^{-8} mol dm^{-3} has been detected. The technique is being developed as an electrochemical detector for liquid chromatography.

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