Spatially resolved infrared spectroscopy: a novel technique for in situ study of spatial surface coverage during CO oxidation on supported catalysts

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A spatially resolved infrared (IR) imaging technique to monitor the linear adsorbed CO coverage on supported catalyst surface combining an IR bandpass filter and an IR thermography camera has been developed. Images acquired during the CO adsorption/desorption and ignition indicate that the technique provides an excellent method to image the change of surface coverage with a spatial resolution. It is expected that the combination of infrared thermography with spatially resolved imaging of surface coverage will provide a deeper insight in the dynamics of spatio-temporal patterns on heterogeneous catalysts.

Keywords: in situ infrared spectroscopy; spatially resolved infrared spectroscopy; CO oxidation on supported catalysts

1. Introduction

In recent years, the studies of spatial temporal oscillations in heterogeneous catalytic systems have received increased attention. The analysis of spatio-temporal patterns on the catalyst surface is critical for understanding the origin and nature of oscillations and other dynamic phenomena occurring during catalytic reactions on noble metals. A variety of different spatio-temporal patterns have been observed on single crystal surfaces under vacuum conditions. Under ultra high vacuum (UHV) conditions, scanning LEED [1] and photoemission electron microscopy (PEEM) [2] have been used to study the patterns and waves of adsorbed species on single crystal surfaces. For reaction on supported catalysts under atmospheric pressure condition, infrared thermography (IRT) has been the most effective technique to examine the development of temperature patterns and the related spatial non-uniformity during reaction. An early study using selective area FTIR with local temperature measurement revealed a spatially non-uniform transition between high and low steady state in CO oxidation on Pt supported catalysts [3]. This method however, has a low spatial resolution. The use of the IRT technique in catalysis was introduced by Schmitz et al. [4,5] to demonstrate the spatial inhomogeneity of the catalyst surface temperature. Further studies using the IRT technique in various exothermic catalytic reaction systems at atmospheric pressure have been performed by Wolf and coworkers [6–8] and Luss and collaborators [9–12]. These studies have provided detailed information and analysis about the spatio-temporal behavior of temperature patterns on various types of catalysts. The IRT technique was also successfully used to control the temperature pattern oscillations during CO oxidation on supported catalyst [13,14]. However, although the IRT studies demonstrate in detail the temperature distribution on the catalyst, it does not provide information about the spatial change in surface coverage, which is an important factor to understand the spatio-temporal dynamic behavior in heterogeneous catalytic reactions. During CO oxidation under UHV conditions, scanning LEED and PEEM measurements have clearly shown the existence of different stationary patterns as well as moving waves of the CO and O_2 surface coverage on single crystal faces. We are not aware of publications reporting the development of the spatial distribution of the surface coverage at atmospheric pressure except for the early study by Kaul and Wolf [3]. Hence, there is a need for an in situ technique with spatial resolution to monitor the coverage of adsorbed species on surfaces of supported catalysts under atmospheric pressure.

In this paper, a spatially resolved infrared imaging technique, which measures the linear adsorbed CO surface coverage in situ, is developed based on the IRT experimental system. The methodology, apparatus and preliminary results are presented in this paper.

2. The methodology

Our earlier study with IRT has shown that the cooling and re-ignition process during the self-sustained oscillations in CO oxidation over Rh supported catalyst wafer occurred with strong spatial inhomogeneity [14]. Re-ignition started from a point downstream and a thermal front propagated upstream to ignite the whole wafer. To obtain a better understanding of the surface process

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during the oscillations, an in situ FTIR study was performed under the same reactor conditions as the oscillations with a moving pattern. A typical spectrum is shown in fig. 1. Spectrum 1 was acquired at the low reaction state during the oscillation and spectrum 2 at the high reaction state. The bands in spectrum 1 from left to right correspond to gas phase CO_2 (2363 cm^{-1}), gas phase CO (2173 cm^{-1}), dicarbonyl CO (2092 and 2029 cm^{-1}), linear CO (2060 cm^{-1}) and bridged bonded CO (~ 1890 cm^{-1}). During the oscillations, the linear and bridged CO bands appeared and increased as the CO_2 concentration decreased, which was accompanied by a cooling process as shown in the IRT patterns [14]. These bands disappeared when re-ignition occurred which was accompanied by a temperature increase. The band of linearly adsorbed CO (2060 cm^{-1}) changed much more dramatically during the oscillations than the other bands which indicated that the linear CO band was related to species active in the oscillations. Since the IR thermographs show strong spatial non-uniformity during the oscillations, it is expected that changes in the linear and bridged CO also occur with some spatial distribution. However, the FTIR technique only measures the average CO adsorption over the whole beam area (about 1 cm diameter) with no spatial resolution.

The FTIR and IRT results, particularly the large difference in the linear adsorbed CO bands between high and low reaction states, suggested that it might be possible to use the spatial capabilities of the IRT experimental system to map up the spatial distribution of linear CO coverage on the surface of a thin catalyst wafer. The optical system in the IRT camera scans over the object point by point at a high frequency such that a radiation intensity image is formed in 1/6 s. The spectral response of the indium antimonide (InSb) photovoltaic IR detector in the IRT camera ranges from wavelengths of 3.5 to 5.6 μm, corresponding to wavenumbers from 1785 to 2857 cm^{-1}. The linear CO (2060 cm^{-1}) band falls within the spectral response range of the IR detector. Meanwhile, the high sensitivity of the IRT camera, which is 0.1°C for a 30°C object, shows that it is capable of distinguishing small changes in the radiation intensity. Therefore, if only the radiation with the wavenumber near 2060 cm^{-1} is allowed to reach the camera, the resulting image would map the spatial distribution of the linear adsorbed CO on the catalyst surface.

The above considerations suggested that imaging the linear adsorbed CO surface coverage with the IRT system can be realized by using a narrow bandpass IR filter with the central wavenumber at 2060 cm^{-1}. In addition, a high temperature external IR source is needed to provide a high intensity IR beam that is transmitted through the whole area of catalyst wafer and the IR filter before reaching the IRT camera. Since linear bonded CO absorbs IR radiation at the wavenumber of 2060 cm^{-1}, the intensity of the IR beam at 2060 cm^{-1} changes after being transmitted through the wafer according to the linear bonded CO concentration. Thus the filtered IR images detected by the IRT camera contain information about the surface concentration of linear CO on *every* point of the wafer. A map of the absorbance which is proportional to the surface concentration could be constructed after image processing. When the temperature of an IR source is at 1100°C, the intensity of the radiation from the source in the narrow wavelength window of 4.78–4.97 μm (2037–2092 cm^{-1}) is 200 times higher than that from an object at room temperature in the 3.5–5.6 μm range. Thus the intensity of this IR beam should be detected after being transmitted through the thin wafer and a band pass IR filter. Moreover, the intensity of the self-radiation from the catalyst wafer during the reaction (at about 100–150°C) in the range of 4.78–497 μm is also much weaker (~ 1%) than that of the beam from the IR source in the same wavelength range. Thus it is expected that the intensity changes in the after-filter image caused by temperature oscillations at the catalyst surface is much smaller when compared to the intensity changes due to changes in linear adsorbed CO surface coverage.

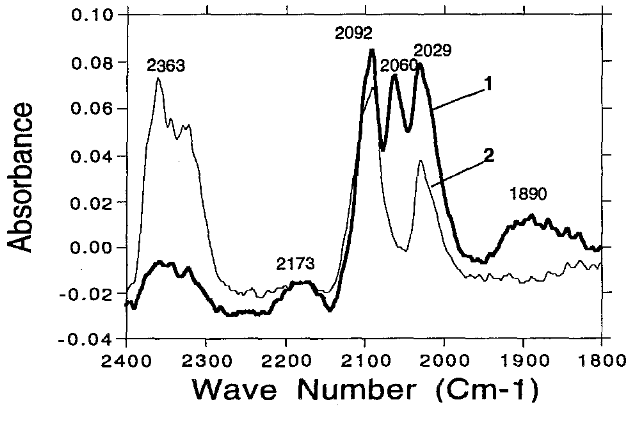


Fig. 1. FTIR spectra during the CO oxidation on the 5% Rh/SiO_2 catalyst wafer. (1) Low state during the oscillations, (2) high state during the oscillations.

3. Experimental system

Apparatus: The diagram of the experimental system is shown in fig. 2. The IR beam pass through the IR transparent reactor windows (CaF_2), the thin catalyst wafer, and the band pass filter to reach the AGA 782 infrared camera. The filament of the IR source is made of a Ni–Cr wire heated by a current to about 1100°C. A parabolic IR reflector with a diameter of 2 inches is used to columnate the radiation from the filament to form a beam. A one inch diameter band pass IR filter with center wavelength at 4.854 μm (2060 cm^{-1}) and half peak band width 0.124 μm (2034–2087 cm^{-1}) is used to cut off the radiation with other wavelengths. The frequency shift of linear CO band between high and low states is

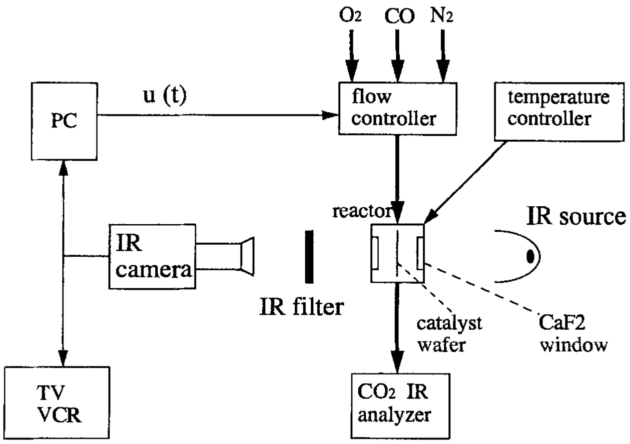


Fig. 2. The diagram of the experimental system.

very small compared to the width of the narrow bandpass IR filter. The IR beam throughput at 4.854 μm (2060 cm^{-1}) is 65%. A 2 cm diameter, very thin (~ 100 μm), 5% Rh/SiO_2 wafer is placed in the center of a continuous flow reactor, in which the feed gases flow over the surface of the catalyst wafer from the top left to the bottom right corner. A PC controlled flow controller (PF914) regulates the flow rate of feed gases. The CO_2 concentration at the reactor exit is measured by an infrared analyzer (Beckman 856). Two heaters, two thermocouples and a temperature controller (Omega CN76000) are used to keep the reactor temperature constant. The AGA 782 IR camera is focused on the surface of the catalyst wafer through the CaF_2 window. As previously mentioned, the InSb detector and the optical scanning system in the camera measure the radiation intensity from the wafer surface point by point and construct an image with 105 × 68 pixels, corresponding to a spatial resolution of 0.2 mm horizontally and 0.3 mm vertically, in 1/6 s. The images thus collected are displayed on an on line TV for in situ monitoring the surface and recorded by a VCR, while digitized and saved in an on line IBM PC.

Catalyst: A 5% Rh/SiO_2 catalyst was prepared by impregnation of the SiO_2 powder with an aqueous solution of $Rh(NO_3)_3$ until incipient wetness. After drying, the powder was calcined in O_2 at 300°C for 1 h and reduced in H_2 at 320°C for 6 h. 50 mg of the catalyst power was pressed at 8000 psia to form a thin wafer of about 2.5 cm diameter. After being placed into the reactor, the catalyst wafer was pretreated in situ in an O_2/N_2 mixture at 220°C for 1/2 h followed by reduction in H_2/N_2 at 240°C for 6 h before each experiment. Ultrahigh purity N_2, O_2, CO and H_2 were used in the experiments.

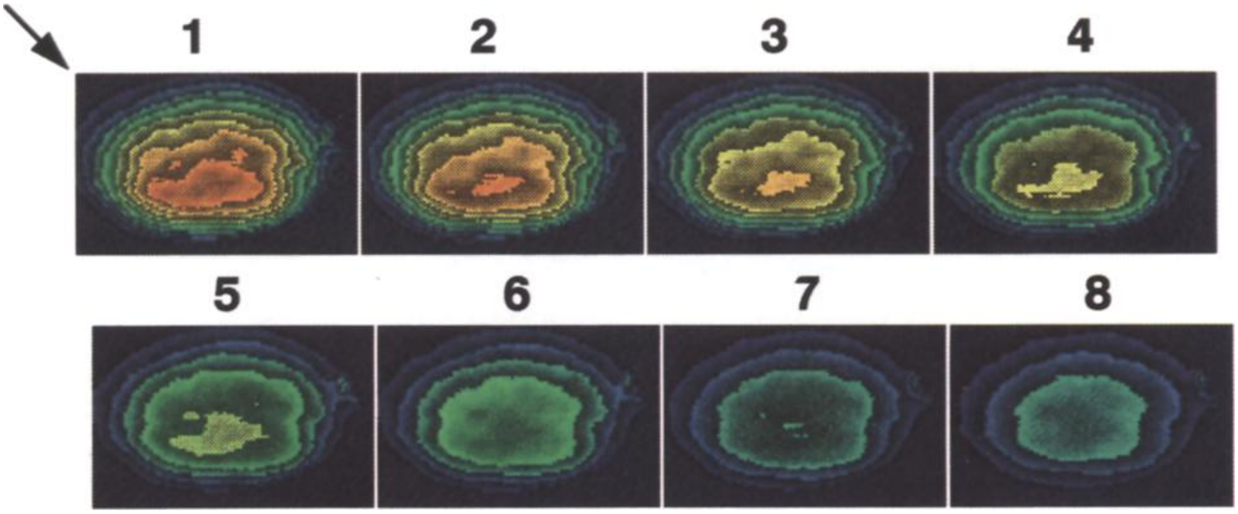
4. Results and discussion

Results using the spatially resolved infrared (SRIR) technique to monitor the CO adsorption/desorption and the ignition are shown in figs. 3 and 4. The surface coverage IR images are presented in different ways: (1) *Original images:* These are the images shown on the screen of the on-line monitor or acquired by the computer. However, the non-uniformity in the wafer thickness and the IR beam intensity will induce non-uniformity in these images. (2) *Difference images:* These are obtained by subtracting the digitized data of another image, such as a clean surface image or a steady state image, from the original images. The difference images demonstrate the changes in the surface coverage more effectively. (3) *Absorbance map:* The absorbance A, which is calculated as $A = \ln[I_c/I]$, is proportional to the concentration of adsorbed CO. I and I_c are the IR beam intensity after being transmitted through the catalyst wafer with and without adsorbed CO, respectively. The ratios of $I_c(x, y)/I(x, y)$ at every point of the wafer can be obtained by processing the digitized original image and the digitized background image of a clean surface (no CO adsorbed). Thus, a map of the absorbance $A(x,y) = \ln[I_c(x,y)/I(x,y)]$ of the whole wafer can be obtained which is proportional to the surface CO concentration distribution. (4) *Image index:* The average of all the digitized data in an image is called the *image index* of this image. The image indexes of a series of images are often plotted vs. time to show how the linear CO surface coverage changes with time globally during a specific process.

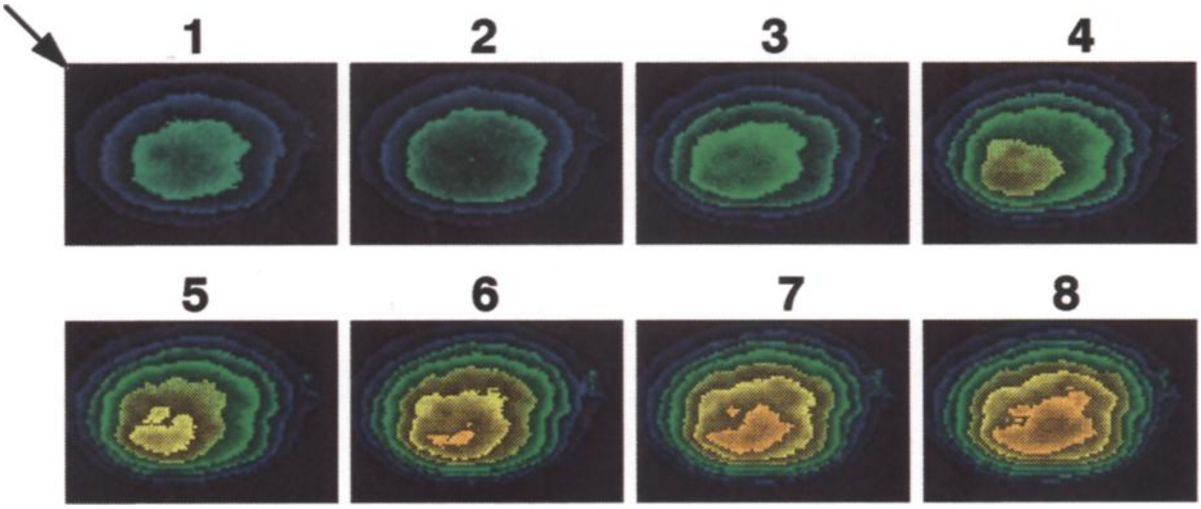
CO adsorption and desorption: Fig. 3a shows the original images acquired during the CO adsorption process. The first panel was acquired when only N_2 was flowing in the reactor. Then, 2 cm^3/min CO was added into a 90 cm^3/min N_2 flow and CO started to adsorb on the catalyst surface. The images on the TV monitor clearly showed that the color of the wafer gradually changed from bright to dark in about 8 min. The change in color was caused by the absorption of the incoming IR radiation by the linear bonded CO molecules on the catalyst surface. Thus the images shown in fig. 3a depict the process of linear CO adsorption on the Rh/SiO_2 catalyst. After flowing CO for 20 min, the CO flow was switched off. As a result, the image color on the TV monitor gradually changed from dark to bright, as CO desorbed from the surface. Fig. 3b shows the images acquired during the CO desorption process. These results clearly indicate that the SRIR technique provides a spatially resolved way to monitor in detail the adsorption and desorption process on a supported catalyst surface.

During the CO absorption and desorption process, there is little change in the temperature of the catalyst wafer. Thus the color changes in the images in fig. 3 are due to the change of linearly adsorbed CO concentration on the surface. The patterns of CO coverage cannot be uniquely ascertained from the original images, however, because the amount of radiation transmitted from the source before CO coverage also depends on the thickness of the wafer. The brightest spot in an image could correspond to a higher intensity region of the incoming radia-

(a) CO adsorption: original images



(b) CO desorption: original images



(c) absorbence maps:

high CO coverage low CO coverage

tion from the IR source, or a thin spot in the wafer which allows more radiation to be transmitted through this area of the wafer. These differences can be eliminated by using *difference images*. The true distribution of CO on the wafer can be obtained after processing the original images by calculating the absorbance at each point on the wafer and constructing the *absorbance map*. Fig. 3c shows two absorbance maps during the CO adsorption process that correspond to the panel 1 and panel 8 in fig. 3b. The transport of CO in the reactor can be monitored by following the frequency corresponding to gas phase CO using a reactor with a blank SiO_2 wafer. A new filter with the center wavenumber at 2173 cm^{-1} must be used, however.

Ignition: Fig. 4 shows *difference images* during the ignition when the reactor temperature was kept at 100°C and the flow rates of CO, O_2 and N_2 were at 0.5, 2.25, and 90 cm^3/min respectively. The difference images are more effective to present a process with rapid changes in the surface coverage, such as the ignition. The surface color was dark at the beginning corresponding to the high CO coverage on the surface. During ignition, which could be easily detected by a sudden dramatic increase in CO_2 production, the original CO coverage image in the TV screen changed from dark to bright. More importantly, it is clearly seen that the color change is not uniform, but started from a point near the outlet of the reactor and it propagated throughout the whole wafer. After ignition, the CO_2 production stayed at the high state and the IR map image stayed in bright color indicating a low CO coverage. The difference images in fig. 4 were obtained by subtracting a low state image from each original image, which was acquired at every second during the ignition process. The bright color region in the difference image means that a large decrease in the concentration of the adsorbed CO occurred in that region during the ignition.

During the transitions between steady states such as the ignition process shown in fig. 4, large changes in temperature and CO coverage occur, so that both the IRT measurement and SRIR measurement can be used to study this process. The CO surface coverage images in fig. 4 show that the ignition starts at a point near the outlet of the reactor, which is consistent with IRT results obtained under similar reaction conditions. It makes sense since in the ignition region the CO coverage decreases while the temperature increases. Further work is underway in our laboratory to study the propagation of thermal front as well as the surface concentration front during the ignition.

It should be noted that the temperature increase in the catalyst surface during ignition could cause a change in the color of the surface coverage images as the thermal radiation from the catalyst wafer within the IR filter window increases. However, since the temperature of the catalyst (110–150°C) is much lower than that of the IR source (~ 1100°C), the self-radiation intensity change due to the surface temperature increase within the filter range is much smaller compared to the intensity of the IR beam absorbed by the linear bonded CO. The temperature error should be considered when the intensity of the IR source is low and the surface temperature change is large. As an example of such case, fig. 5 shows an experiment with a lower IR source temperature while both O_2 and CO concentration are 4.5 times higher than that in the experiment shown in fig. 4 and hence a larger temperature jump occurred at the surface during ignition. In this case, the temperature error can be observed as shown by the image index in fig. 5. The ignition was started by flowing CO into an O_2/N_2 feed at 118°C reactor temperature. Before feeding the CO, the surface temperature is low with no CO adsorbed. Ignition occurred right away when CO was fed into the reactor. Then, the system stayed at a high temperature state, also showing no detectable CO surface coverage. The increase of the SRIR image index from 105 to 110 was thus due to the increase in the surface temperature caused by the exothermic reaction. After ignition, the O_2 feed was stopped which finally resulted in a low temperature and high CO covered catalyst surface as the image index decreased to 87. The decrease in the SRIR image index from 110 to 105 is due to the temperature error and from 105 to 87 is caused by CO adsorption on the catalyst surface. In the case shown in fig. 5, the temperature effect contributed to 20% of the total change in image index during the process. Although the temperature effect cannot be eliminated in the SRIR measurement, it is easy to minimize it just by increasing the intensity of the incoming IR beam with a high power IR source. Alternatively, a series of surface coverage images of the catalyst surface under an inert gas acquired at different reactor temperatures can be used to correct the temperature error on the concentration images according to temperature patterns from the IRT measurements during the same process.

The purpose of this paper is to show the development of the SRIR technique to image the linear CO surface coverage on a supported catalyst. Although the dynamics of CO oxidation has been an active research topic for over 20 years, it is the first time that the spatial distribution of CO coverage on a *supported* catalyst during the reaction can be studied in situ at atmospheric pressure. More importantly, this infrared experimental system is capable of in situ measurements of both the

◀ Fig. 3. (a) and (b) original images during the CO adsorption and desorption process. The time interval between acquiring each image is 1 min. The brighter color indicating a lower CO coverage. (c) The absorbance maps of a high and a low CO covered surface (calculated from panel 1 and panel 8 in (b) during the desorption process). The brighter color indicating a higher CO coverage. The reactor temperature is 118°C. The flow rate of N_2 is 90 cm^3/min. The flow rate of CO during the adsorption experiment is 2 cm^3/min. The flow direction is indicated by the arrow on the first panel of the images.

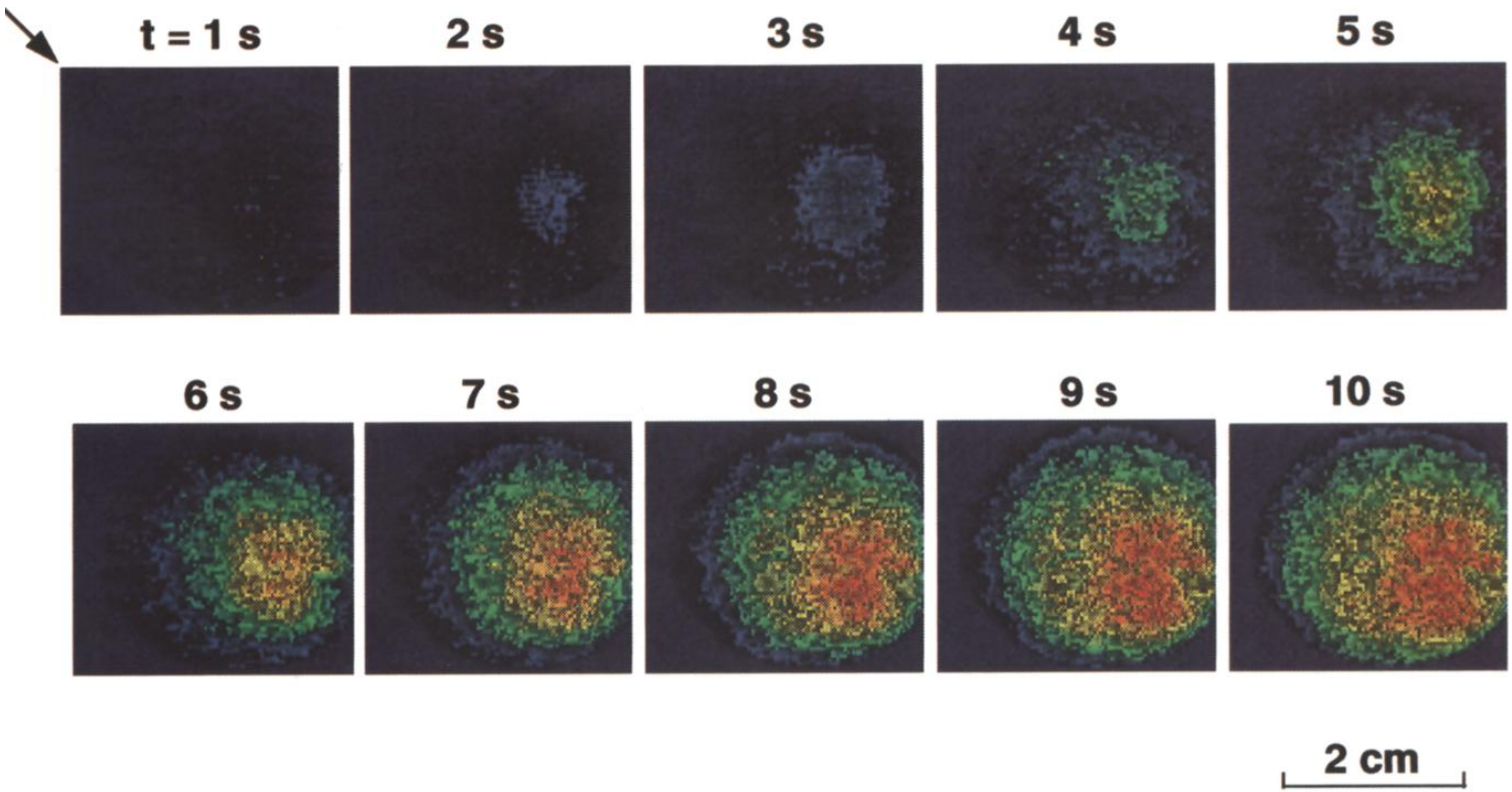


Fig. 4. The difference images obtained by subtracting the digitized data of a low state image from original images, which are acquired in 10 s during the ignition process. The brighter color indicates the lower CO coverage. The reactor temperature is 100°C. The flow rates of CO, O_2, and N_2 are 0.5, 2.25, and 90 cm^3/min respectively. The flow direction is indicated by the arrow on the first panel of the images.

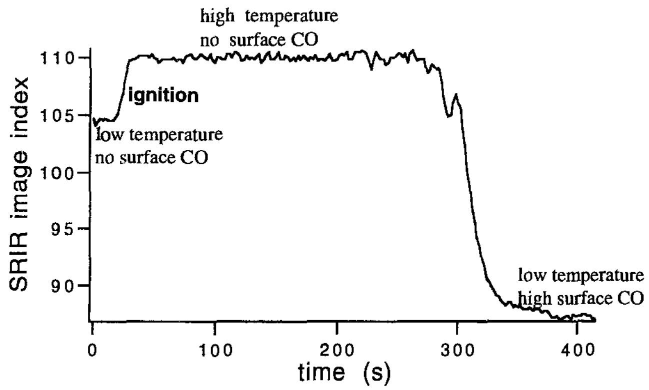


Fig. 5. The image index of the surface coverage images during an ignition and an extinction process when there is a large temperature change at the catalyst surface. The *image index* is the average of all the data on a digitized image. The reactor temperature is 118°C.

temperature and surface coverage images. By removing the IR filter and turning off the IR source, surface temperature patterns and their development are acquired; putting back the IR filter and IR source, the surface coverage patterns and their dynamics can be measured. During thermochemical oscillations on supported catalysts, the spatio-temporal oscillations are affected by thermal coupling and gas phase coupling between different parts on the catalyst. Work is underway in our laboratory using both of these techniques to study the dynamics of both temperatures and surface concentration patterns during CO oxidation.

5. Conclusions

An experimental technique to monitor the linear adsorbed CO surface coverage using infrared filters and an infrared camera has been developed. Images that contain information of the spatial distribution of the CO on Rh supported catalysts are presented. Images acquired during the CO adsorption/desorption and ignition indicate that the technique depicts the surface coverage change with spatial resolution. Coupling of these images with temperature patterns will allow to elucidate the interaction of the various processes involved in self-sustained oscillations on supported catalysts.

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