Rotating Temperature Pulse During Hydrogen Oxidation on a Nickel Ring

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Reaction-diffusion interactions generate spatiotemporal patterns in a variety of *uniformly active* chemical media. It is of interest to know how these patterns are affected by media nonuniformity. Here, we report the first observation of a rotating temperature pulse on a nonuniformly active (i.e., polycrystalline) surface of a nickel ring during atmospheric hydrogen oxidation. The pulse had an amplitude of about 100 °C and completed one cycle around the ring every 565 s. Its width, velocity, and maximum temperature changed during each cycle, but were constant at a given position.

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Numerous numerical and theoretical studies have enlightened our understanding of spatiotemporal patterns [1-4], while experimentalists have been looking for model systems with low spatial dimensionality to confront these predictions with actual measurements and to gain insight into the behavior of more complex systems and geometries. Reaction-diffusion models with either oscillatory or excitable kinetics predict propagating pulses on rings [2,3] reproducing the behavior of many chemical and biological systems. The well-known Belousov-Zhabotinskii reaction [5] has stimulated significant theoretical interest in patterns generated by a chemical reaction in a uniformly active liquid medium. Swinney's group developed a ring-gel reactor that confirmed the generation of rotating waves by the coupling of diffusion and reaction [6]. Later, the Bordeaux [7] and Austin groups [8] developed gel-strip reactors in which Turing patterns were formed by the interplay of a chemical reaction and diffusion. Ertl's group [9] found a variety of spatiotemporal patterns on Pt single crystal surfaces during the low pressure, isothermal catalytic oxidation of carbon monoxide.

It is of intrinsic interest and practical importance to know how the spatiotemporal patterns observed in homogeneous media are modified and distorted in an inherently nonuniform media. So far, the only patterns observed on polycrystalline catalysts were of temperature waves emanating from one or several locally active sites [10-12]. Moving temperature fronts and pulses were observed on electrically heated catalytic wires and ribbons [13-17]. However, analysis [18,19] shows that without electrical heating these temperature fronts would have been unstable in at least some of these experiments.

We report here the first observation of a regular spatiotemporal pattern on a polycrystalline catalyst that is not heated electrically; i.e., rotating temperature waves propagating azimuthally on a polycrystalline nickel ring (3.8 cm outer diameter, 3.2 cm inner diameter, 0.13 mm thick) during the atmospheric oxidation of hydrogen in a reactor (Fig. 1) fed with a mixture of 5% oxygen and 95% hydrogen. In the experiments reported here, the average residence time of the gases in the reactor was 6.6 s.

The instantaneous local infrared radiation intensity of points on the nickel ring was measured by a thermal imager (AGEMA Thermovision 780). Spatial resolution was about 0.3 mm^2, while the thermal resolution was about 0.5 °C. The imager scans the surface 25 times per second, producing a thermal image of 128 columns of 64 points. The data are displayed in real time on a color TV monitor, digitized, and stored on a hard disk. The catalyst was activated by repeated oxidation-reduction steps at 450 °C, as described by Kurtanjek, Sheintuch, and Luss [20].

Experiments conducted at a feed gas and oven temperature of 233 °C revealed a rotating temperature pulse with a period of 565 s. Figure 2 shows six thermal images of the ring at different times, with the white area denoting high temperatures and the black denoting low temperatures. The gradual transition from white to black covers in this case a temperature range of 255 to 390 °C.

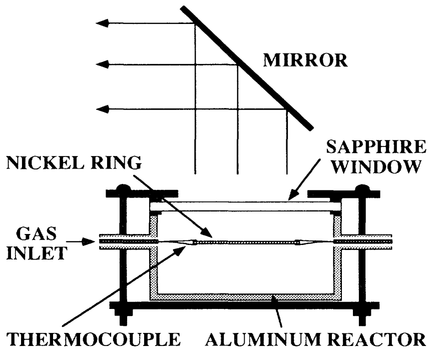

FIG. 1. Side view of the cylindrical (7.6 cm inner diameter by 3.8 cm high) aluminum reactor, which has a 0.32 cm thick sapphire top. The ring was held parallel to the top by four fine thermocouples (0.025 cm) looped through small holes in the periphery of the ring. The reactor was fed via four evenly spaced radial ports and exited through four similar ports positioned 1.3 cm below the inlet ports and shifted aside by 45°. The effluent composition was measured by a mass spectrometer. Tracer experiments showed that the mixing by the jets produced a residence time-density function very close to that of a continuously stirred tank reactor. The reactor was placed inside an oven to control its temperature.

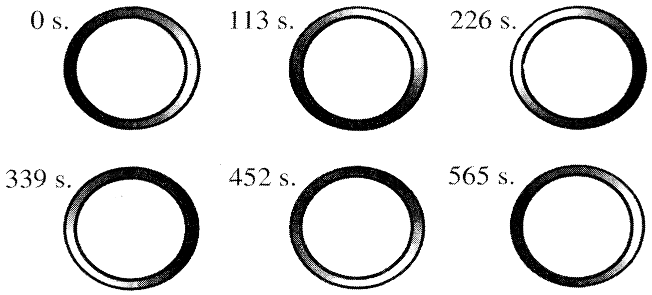

FIG. 2. Six thermal images of the ring, taken over one period of pulse rotation. The transition from white to black corresponds to a temperature range of 390 to 225 °C, respectively. The black rings around each image were added to enhance the contrast, which is much clearer in the original color images.

The images clearly show the motion of the pulse along the ring. The pulse motion persisted with no changes in frequency or amplitude for over 70 h, at which time the experiment was stopped.

An angular position versus time diagram of the infrared radiation intensity (Fig. 3) shows the pulse movement during four complete cycles. It shows that during each cycle the pulse width and the azimuthal pulse velocity (inverse slope of an isotherm in the time versus angular position diagram) vary with angular position, but are constant at any given position. This behavior did not change during the experiment.

The chemical reaction rate is a strong function of the temperature. Thus, the periodic changes in the shape and size of the high temperature pulse led to periodic variations in the reaction rate (Fig. 4). The effluent concentration of the limiting reactant concentration (oxygen) varied from 2.9 to 2.6 vol%, corresponding to a conversion range of 42% to 48%. The effluent gas temperature oscillated between 244 and 254 °C. The oxygen conversion exhibits three maxima per cycle, corresponding to the periodic changes in the size and shape of the pulse. Analysis of the color version of Fig. 3 indicates that the pulse shape changes are caused by different rates of movements of its leading and trailing fronts. The increase in the conversion occurs when the pulse size increases as the leading front moves faster than the trailing one, and vice versa. During the first 140 s shown in Fig. 4, the pulse center moves from angular position 285° to 335°. However, between times of 345 and 420 s in Fig. 4, the pulse center moves from angular position 90° to 165°. Thus, the pulse angular velocity in the second case is 2.8 times that in the first. The time trace of the oxygen concentration oscillations did not change its shape or frequency during the long experiment. These periodic changes in the pulse shape and velocity are a novel feature, which has not been observed or predicted to exist in uniformly active reacting media and is caused by the catalyst nonuniformity.

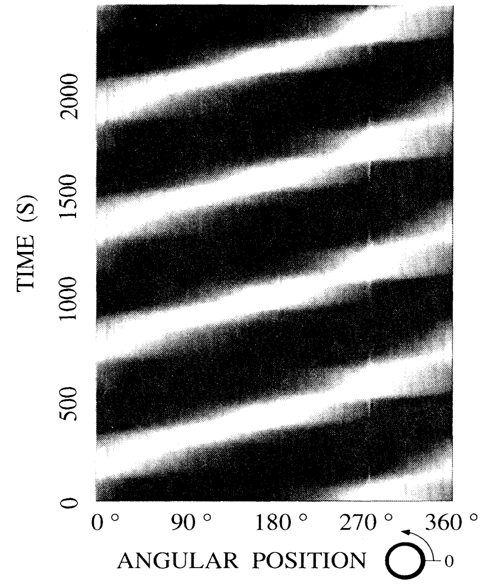

FIG. 3. An angular position vs time diagram of the IR radiation intensity. The white-to-black transition covers the temperature range of 390 to 255 °C. The variation in the horizontal width of the white region corresponds to the periodic changes in pulse length with angular position. Similarly, the changes in the slope of an isotherm (which is not very clear in a black-and-white figure) are proportional to changes in the propagation velocity.

Figure 5 shows the instantaneous temperature profiles at two times. Profile 1 corresponds to $t = 420$ s in Fig. 4 and the pulse center at an angular position of 165°. At this position, the pulse attains its maximum peak temper-

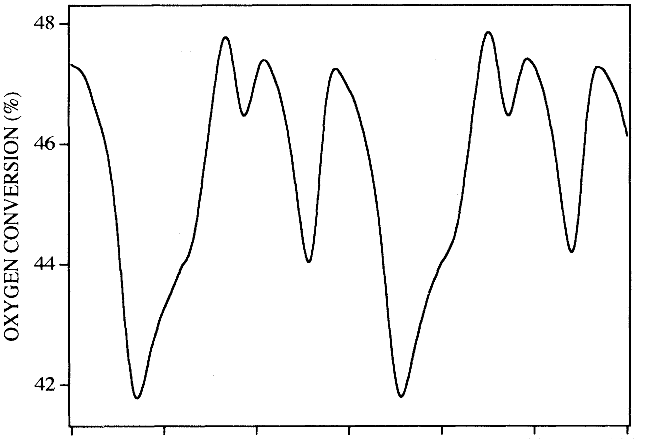

FIG. 4. Periodic oscillations in the oxygen conversion in the reactor. The first three maxima in the conversion correspond to the pulse center at angular positions of 285°, 90°, and 165°. The first three minima are of the pulse center at 335°, 135°, and 215°.

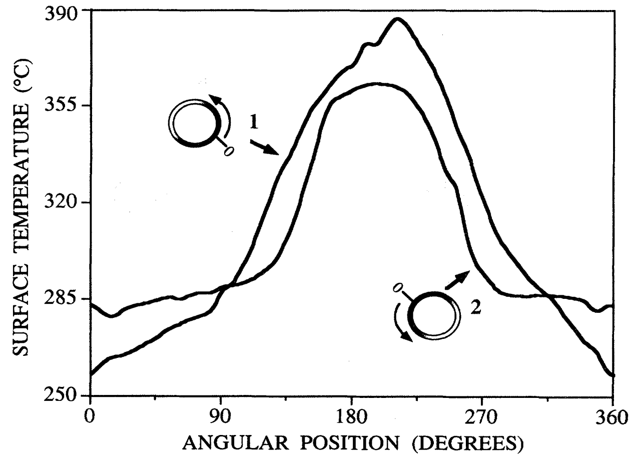

FIG. 5. Temperature profiles corresponding to times of 420 s (1) and 140 s (2) in Fig. 4. The pulse center is at angular positions at 165° (1) and 335° (2). Profile 1 has the highest peak temperature of any pulse and the longest temperature front. This pulse occupies essentially the whole ring. Profile 2 has a long uniform high-temperature section but is the shortest pulse, occupying only one-half of the ring length.

ature and length, occupying essentially the whole ring. Profile 2 corresponds to $t = 140$ s and an angular position of 335°. Here, the pulse attains minimal length and amplitude, occupying only about half of the ring. However, it has a long uniform high-temperature section. The temperatures of the low-temperature section of profiles 1 and 2 differ by about 15 °C. The difference between the peak and lowest temperature on the ring is about 130 and 85 °C for profiles 1 and 2, respectively. We believe that these periodic changes in the pulse features with azimuthal position are due to the nonuniform catalytic activity of the ring.

The observation of a rotating temperature pulse on a polycrystalline surface at atmospheric conditions suggests that other and more intricate spatiotemporal patterns exist on the surface of commercial catalysts. It is important to gain an understanding of the chemical reactions, operating conditions, and catalyst geometries that generate such spatiotemporal patterns, and of the impact of the nonuniform catalytic activity on these patterns. It is of particular importance to gain an understanding of the impact of these spatiotemporal patterns, and in particular if they may lead to a product distribution which is not attainable on a uniform catalytic surface. The rotating pulse on a ring may serve as a useful model system for testing the difference in the dynamic motion in a uniform and nonuniform media and as a guide in the development of mathematical models predicting the behavior of such systems.

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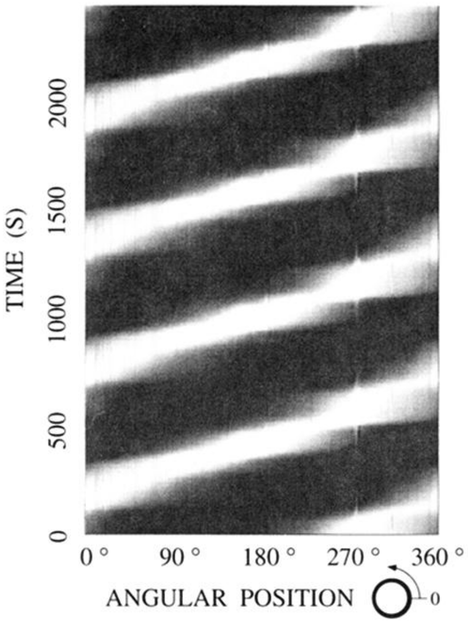

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