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COUPLED OSCILLATIONS OF $H_2/O_2/CO$ ON SILICA SUPPORTED RHODIUM CATALYST

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Self-sustained oscillations obtained during the catalytic oxidation of CO and H_2 were studied over Rh/SiO_2 by an FTIR-mass spectrometric technique. An average oscillatory period of 7.1 ± 0.5 minutes was obtained for the CO/O_2 reaction at 348 K. For the H_2/O_2 oscillatory reaction the period was observed to be 1.3 ± 0.8 minutes. When the oscillations were coupled at the same temperature, the period for both the CO/O_2 and the H_2/O_2 reactions was observed to be 7.9 ± 0.8 minutes. The kinetic coupling of the reaction rates is explained by considering the periodic fluctuations in surface temperature which occur as a result of the more exothermic CO/O_2 reaction.

Oscillatory behavior in chemical reactions has been the subject of considerable interest not only within the catalytic community but also in reactions which occur in the liquid phase. A very large number of reactions have been shown to exhibit oscillatory behavior and it is not our purpose here to review the very extensive literature on this subject. For the interested reader the authors recommend a recent review by Razon and Schmidt [1] which deals with oscillatory behavior in heterogeneous systems and a recent review by Stein et al [2] who have outlined oscillatory reactions in homogeneous systems. In all of these studies, the kinetics of the reacting system plays a central role in understanding why reactions exhibit self-sustained oscillations. The authors are of the opinion that a large number of the experimental observations; i.e., surface and adsorbate phase changes, mass transfer effects, heat transfer effects, and fluctuations in surface temperature occur as a result of reaction kinetics. In order to focus specifically on this aspect the authors have attempted to couple the oscillatory behavior of two reactions which independently exhibit self-sustained oscillations. These two reactions are the oxidation of H_2 and CO.

The study reported here makes use of an *in-situ* infrared cell reactor which has been described in the literature [3]. A block diagram of the associated components used in the flow system is outlined in fig. 1. The reactor was placed in the

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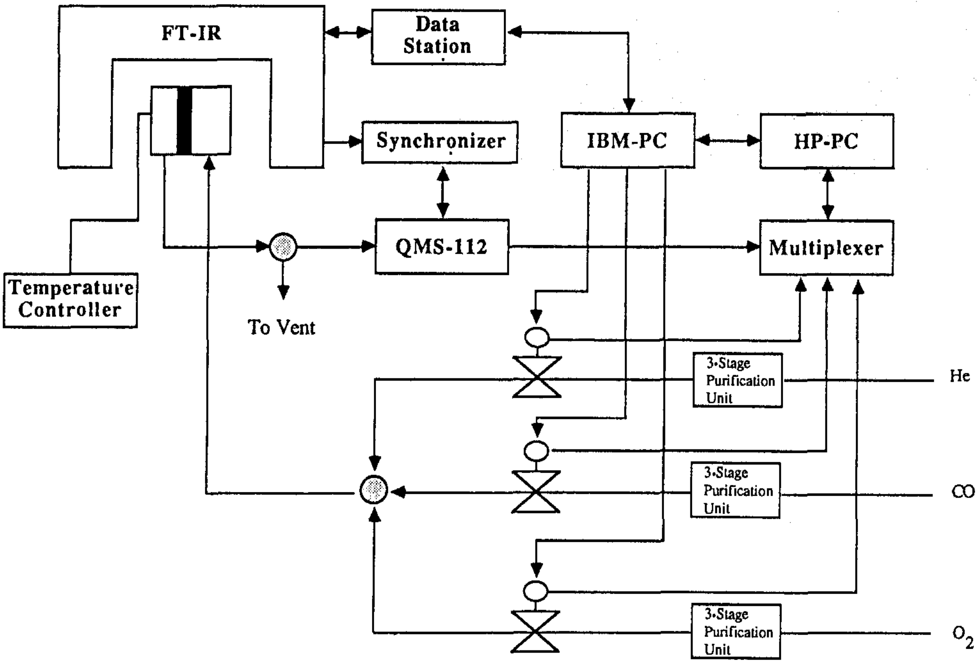

Fig. 1. Diagram of the flow system.

sample chamber of an FTIR (FTS 40, Digilab) spectrometer. The gas phase composition in the reactor was monitored by a quadrupole mass spectrometer (QMS 112, Balzers). A synchronizer was designed in our laboratory to coordinate the scanning of the FTIR and the QMS. The infrared data were processed using a 3240-SPC Data Station (Digilab) and could be transferred to a personal computer (IBM-AT). The mass spectral data were collected and analyzed in the IBM-AT. The temperature of the reactor was controlled by a temperature programmer (Valley Forge Instruments Inc., Model PC 6011). The temperature gradient between the inside and the outside of the reactor was observed to vary between 10 and 50 K depending upon reactor temperature. All of the temperatures reported here were gas phase temperatures measured inside the reactor.

The silica-supported Rh catalysts were prepared by wet impregnation. Initially, the appropriate weight of $RhCl_3 \cdot 3H_k2O$ (Strem Chemical) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. The solutions were mixed with Cab-O-Sil, grade M-5 (Cabot Corp., Boston, MA), until a slurry having the consistency of a thin paste was formed. The surface area of Ca-O-Sil, as reported by the manufacturer, was 200 m^2/g. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The metal loading was 3 wt%. The dried catalyst was then ground into a fine powder, less than 45 μm, and pressed into self-supporting disks with an optical density of approximately 80 mg/cm^2.

The gases used in this study were subjected to the following purification treatment: H_2 and He (ultrahigh purity, Linox Co., Illinois) were further purified by passing them through a deoxo unit to convert O_2 impurities to H_2O, which was then removed by a molecular sieve maintained at 193 K by means of a dry ice-acetone trap. It was then passed through an MnO trap which had been activated in flowing H_2 at 773 K. The moisture in CO and O_2 (ultrahigh purity, Linox Co., Illinois) lines were removed by dry ice-acetone traps.

Gas flow rates were controlled by using Tylan (model FC260) electronic flow controllers. The flow controllers were calibrated by the manufacturer using gas mixtures which were identical with those used in this study. The calibration was rechecked in our laboratory by means of a bubble flow meter and a gas chromatograph.

Chemisorption measurements were performed by using the dynamic pulse method [4]. Metal dispersion was calculated on the basis of a CO/Rh(s) adsorption ratio of 1 and found to be 43%. The CO/Rh(s) ratio of 1 is only valid when the surface concentration of the CO dicarbonyl species is small, as is the case for well-reduced Rh/SiO_2. For the case of Rh/Al_2O_3 or for very highly dispersed Rh catalysts this assumption is not valid [5].

The freshly pressed sample disks were reduced according to the following schedule: The catalyst was exposed to flowing He (100 ml/min) at 323 K. The temperature was then increased at a linear rate of 10 K/min to 423 K in flowing He and maintained at 423 K for 0.5 hr. The He flow was switched to H_2 (100 ml/min) at 423 K and the temperature was then increased at 10 K/min to 728 K. The catalyst was reduced in flowing H_2 for 3 hr at 728 K followed by treatment in flowing He for 0.5 hr at the same temperature. The temperature was then reduced to 323 K in flowing He.

The procedure used to initiate oscillatory reaction conditions has been extensively described by Sharma et al. [6] and by Kaul and Wolf [7]. Briefly, the reaction temperature is ramped from 323 K to the ignition temperature (~ 473 K). The temperature programmer is then turned off and the reactor is allowed to cool in a constant flow of CO and O_2. When the infrared bands reappear and begin to show unstable behavior, the reaction conditions are set and the self sustained oscillations are followed. In this study a CO/O_2 partial pressure ratio of 1.8 was used.

Catalyst temperature fluctuations, which were observed during the self-sustained oscillations, were measured by calibrating the temperature dependent features associated with the longitudinal and transverse bands of SiO_2 centered at 1405 and 1475 cm^{-1}. This procedure has been extensively described by Sharma et al. [6]. It is shown in fig. 2 that the support temperature fluctuates between 383 K and 463 K, when the gas phase temperature 248 K. Unfortunately this procedure could not be followed for temperature fluctuations for the oxidation of H_2 or the coupled oscillations due to the interference of chemisorbed H_2O in the spectral region of interest. Hence, all the temperatures reported here are gas phase temperatures.

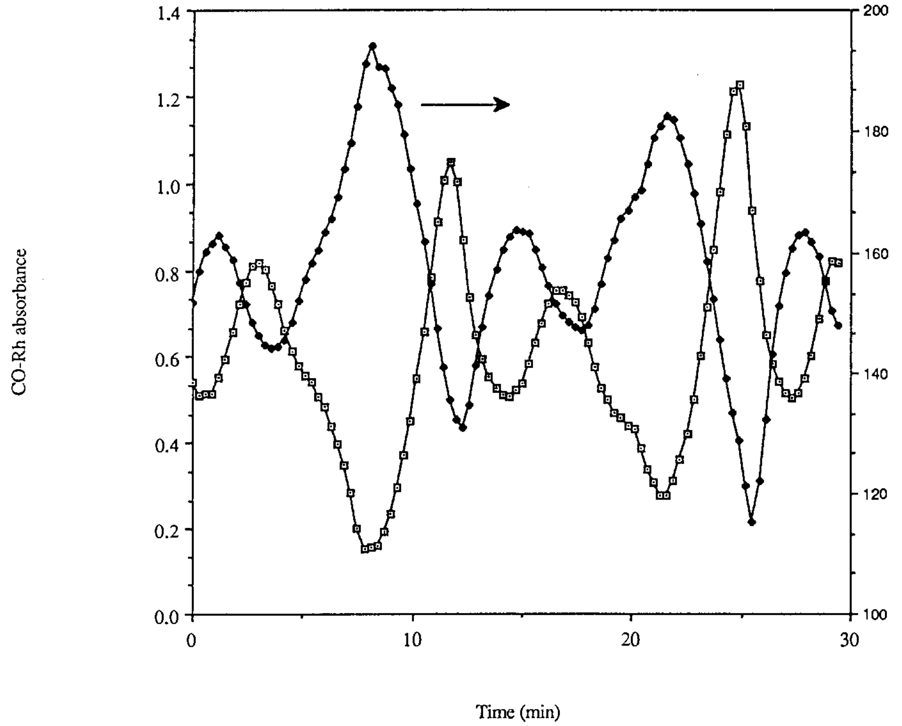

Fig. 2. Infrared absorbance (2040 cm^{-1}) and surface temperature during the self-sustained oscillations of the CO oxidation reaction (348 K, total flowrate = 100 ml/min, $CO/O_2 = 1.8$, He flowrate = 80 ml/min).

Because self-sustained oscillations for the oxidation of H_2 were easier to initiate than those obtained for the oxidation of CO, CO oscillations were first initiated by the method previously described. H_2 was then admitted to the system and the resulting oscillatory behavior was followed using a quadrupole mass spectrometer to follow H_2O and CO_2 formation in the gas phase. Fluctuations in the surface coverage of CO were followed using FTIR to determine the absorbance of the CO stretching frequency centered at 2042 cm^{-1}. Under the conditions of this experiment, there was the only linear CO species adsorbed on the surface under reaction condition. The dicarbonyl species was not present [8]. A partial pressure ratio of $(CO + H_2)/O_2 = 2$ was used throughout.

The self-sustained oscillations for the oxidation of CO together with the fluctuations in surface temperature are shown in fig. 2. It is important to note that the maximum catalyst temperature is coincident with the maximum rate of formation of CO_2 and a minimum surface coverage of CO. The self-sustained oscillatory behavior for the oxidation of H_2 is shown in fig. 3 in which the mass signal of H_2O is plotted as a function of time. The coupled oscillations are shown in fig. 4.

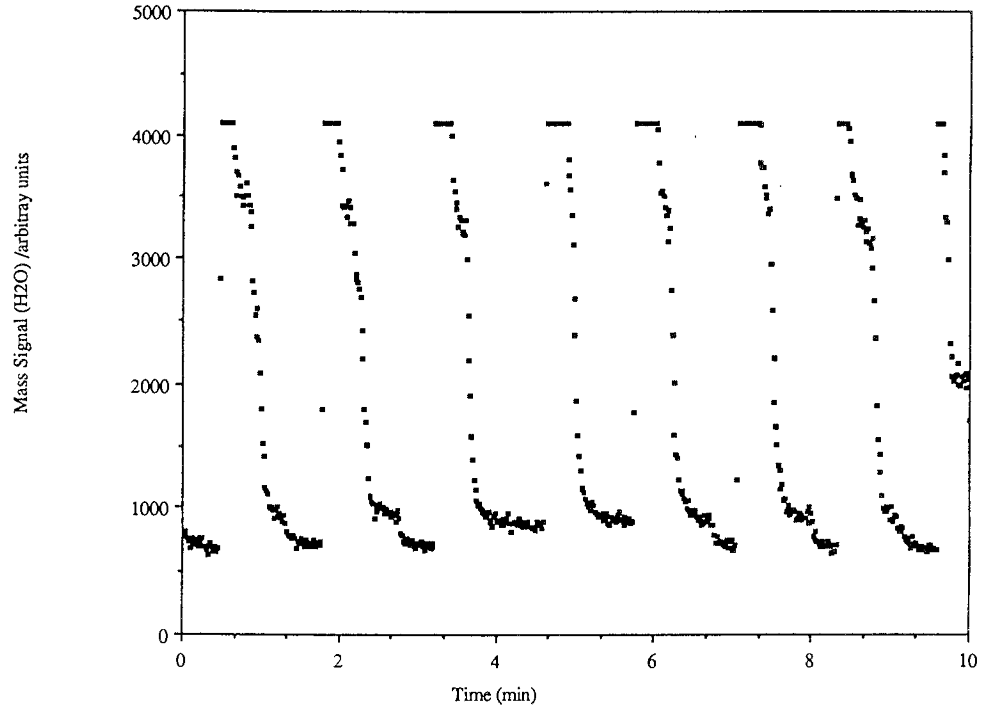

Fig. 3. Mass spectrometer signal of water during the self-sustained oscillations of H_2/O_2 reaction (355 K, total flowrate = 100 ml/min, H_2/O_2 = 1.8, He flowrate = 80 ml/min).

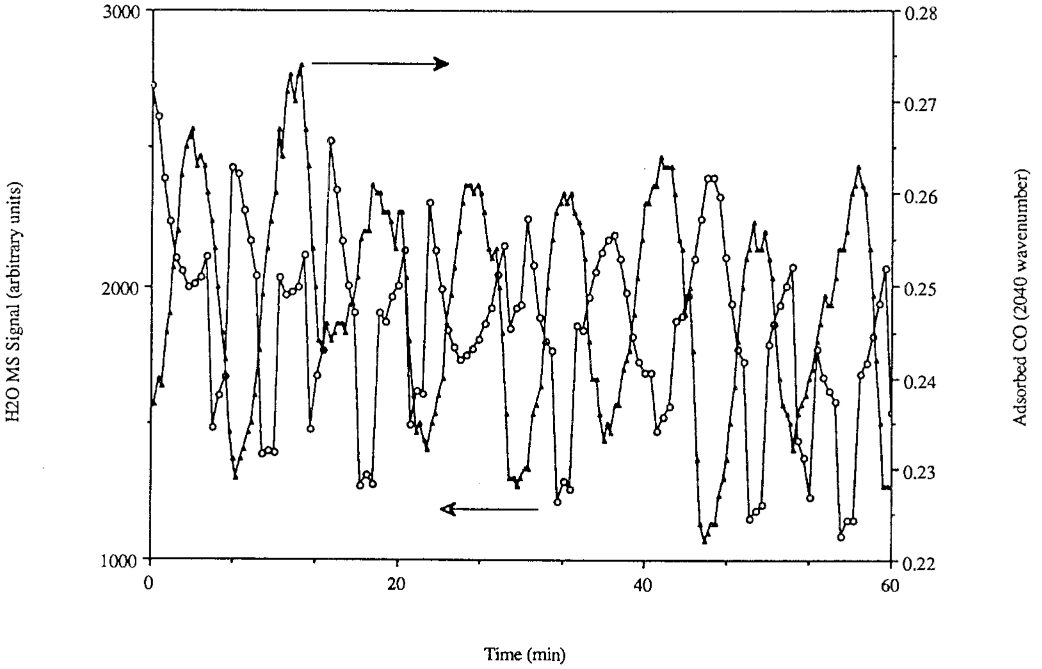

Fig. 4. Infrared and mass spectra corresponding to the coupled self-sustained oscillations of $H_2/O_2/CO$ reaction (355 K, total flowrate = 100 ml/min, $(CO+H_2)/O_2$ = 2, He flowrate = 80 ml/min).

Table 1
Periods of oscillation

Reagents	Products	Gas phase temperature (K)	Periods (min)
CO/O_2	CO_2	248	7.1 ± 0.5
H_2/O_2	H_2O	355	1.3 ± 0.8
$CO/O_2/H_2$	CO_2	355	7.9 ± 0.8
	H_2O	355	7.9 ± 3.1

Table 1 summarizes the results of the coupled oscillations of $H_2/CO/O_2$. At 348 K the average period of the CO/O_2 oscillation reaction is 7.1 ± 0.5 minutes, while that of the H_2/O_2 oscillations is almost six times shorter than that observed for CO/O_2 (1.3 ± 0.8 min). When the oscillations were coupled at the same temperature, the period observed for the formation of CO_2 remains about the same (7.9 ± 0.8 min). However, the oscillatory period for the reaction of H_2/O_2 increased and coincided with that observed for CO_2 formation (7.9 ± 3.1 min). This suggests that the kinetics of the oxidation of CO drives that of the oxidation of H_2. It is in the authors' opinion that, due to the CO oxidation reaction, the fluctuation of the surface temperature drives the reaction of H_2O oscillations.

A brief explanation for our observations is as follows: at a high surface coverage of CO, the reaction rate is a minimum because the reaction is inhibited by adsorbed CO. Under these conditions, the surface temperature is also a minimum. At this point, O_2 adsorption begins to increase and the reaction rate also increases until the surface coverage of CO is a minimum. Simultaneously the surface temperature also increases to its maximum value. As the surface coverage of CO is depleted by reaction, both the rate and the surface temperature begin to decrease thus completing the oscillatory reaction cycle. The exothermicity of the reaction then drives the H_2 oxidation reaction in such a way that the rate of the H_2 oxidation is in phase with the surface temperature and thus with the oxidation of CO. The exothermicity of the reactions differ by about 10 kJ/mole with the CO oxidation being the more exothermic of the two.

Acknowledgements

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