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RESEARCH NOTE

Spectroscopic Identification of the Active Site for CO Oxidation on Rh/Al_2O_3 by Concentration Modulation *in situ* DRIFTS

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Diffuse reflectance infrared spectroscopy experiments are described in which the concentrations of the reactant gases passing over a solid catalyst are modulated. This simple modification to the normal *in situ* experiment enables direct correlation of specific surface species with the production of gaseous products. Spectra of solely the active surface intermediates with no contribution from so called "spectator" species are generated. For CO oxidation over a Rh/alumina catalyst at 576 K, the active CO species is identified as linearly adsorbed CO on oxidized Rh sites ($\upsilon_{CO} = 2100\ cm^{-1}$) on a catalyst surface apparently otherwise dominated by CO adsorbed as unreactive geminal dicarbonyl. © 1999 Academic Press

Key Words: **rhodium; CO oxidation; forced oscillations; DRIFTS.**

INTRODUCTION

In-situ IR spectroscopy of species adsorbed on catalyst surfaces is a valuable tool in understanding catalytic processes (1). A significant shortcoming of this technique is, however, the difficulty in determining which species are playing an active role in the catalysis and which are merely spectators. The presence of an absorption band of some surface species, even when spectra are recorded under reaction conditions, is never a reliable indicator of the relevance of that species to the ongoing catalysis (1). To overcome this, transient techniques are often employed and generally involve observation of the effect of flow switching (2) or pulse adsorption (3). Periodic cycling of the inlet composition is an established method of operating catalysts under non-steady-state conditions in order to obtain improvements in product yields and selectivities over steady-state conditions (4). This approach has been combined with *in situ* infrared spectroscopy to study the $NO/CO/O_2$ system on Pt/Al_2O_3 (5). The dynamic response of CO_2 methanation over Ru/TiO_2 to periodic variations in the CO_2 feed has been followed by both mass spectrometry and DRIFTS to obtain information on the kinetics and mechanism of reaction (6). The concentration modulation technique described here is a novel refinement of this approach capable of producing IR spectra in which the presence of bands from an adsorbed intermediate are a good indicator of its role in the catalytic reaction.

METHODS

The catalyst used in this work was a 2% Rh/Al_2O_3 sample supplied by Johnson Matthey. This was characterized by chemisorption measurements carried out on a Micromeritics ASAP 2010C. Hydrogen chemisorption on the reduced catalyst allowed determination of the metal surface area as 3.9 m^2/g, which corresponds to a dispersion of 45%. This was consistent with CO chemisorption measurements provided that a CO : Rh ratio of 2 was assumed.

CO (99.95% Linde) and O_2 (99.5% Linde) were admitted to a mixing volume, consisting of 1.5 m of 5-mm-i.d. tubing, at rates determined by electronic flow controllers (MKS). This gas mixture then passed through a solenoid control valve before being added to a helium diluent stream also regulated by a mass flow controller. The control valve was driven from a square wave function generator with a DC offset on the waveform providing the set point for the average flow of the reactant gas and the amplitude, allowing control of the degree of modulation of the composition.

The diffuse reflectance infrared spectroscopy (DRIFTS) cell was an in-house design, details of which have been published elsewhere (7). Spectra were measured with a BioRad FTS 6000 spectrometer equipped with a SpectraTech diffuse reflectance optics and a narrow band MCT detector. The gas exiting from the cell was sampled through a fused

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silica capillary coupled to a quadrupole mass spectrometer (MS) (LedaMass). This system has been designed for full frequency response DRIFTS studies (7, 8), where the response of both the gas and the surface phase to modulation of reactant concentrations in the range 0.02 to 4 Hz can be followed to allow investigation of the surface kinetics. In this instance, however, a single modulation frequency of 0.11 Hz was employed to illustrate the advantages of simple concentration modulation in *in situ* DRIFTS experiments. The inlet gas composition to the DRIFTS reactor was 5%CO : 3%O_2 in He at a total flow rate of 65 sccm with ±40% modulation of the combined CO and O_2 flow.

Approximately 30 mg of the catalyst was first introduced into the DRIFTS cell in the calcined state and then allowed to equilibrate under a constant flow of the reactant gas stream at the operational temperature. During the catalyst run in, MS data was used to measure conversion while DRIFTS spectra gave an indication of the surface composition of the catalyst. These DRIFTS spectra were produced from 4 cm^{-1} resolution single beam spectra recorded during equilibration ratioed against a background single beam spectrum of the Al_2O_3 catalyst support. Thereafter, during modulation of the gas stream at 0.11 Hz, spectra were collected at a rate of 5.2 Hz using the kinetics software of the WinIRpro 2.6 package associated with the FTIR spectrometer using a background recorded at equilibrium under the constant gas flow just prior to modulation of the gas stream. The spectra were again recorded at 4 cm^{-1} resolution with each spectrum representing one individual scan. MS data measuring the exit gas composition was collected in synchrony with the DRIFTS data.

RESULTS AND DISCUSSION

Figure 1 shows a representative DRIFTS spectrum at 567 K after the sample had been heated from room temperature and equilibrated under the reaction mixture. At this temperature the rate of CO_2 production was 18 μmol $m^{-2} s^{-1}$, corresponding to ~60% conversion of CO. For adsorbed CO, the two bands of roughly equal intensity at 2081 and 2010 cm^{-1} can be assigned to a geminal dicarbonyl species (9). There is also a weaker feature at 1880 cm^{-1} consistent with CO in bridged sites. There is no obvious band that would be associated with linear CO on Rh metal; however, this could be partly obscured by the lower of the two dicarbonyl peaks. In general the CO features are broadly similar to what would be expected for a low metal loading Rh/Al_2O_3 catalyst (10). Due to the low path length of the cell and the relatively high conversion there is no CO gas phase signal from the 5% inlet concentration. The most substantive feature in the spectrum is the broad maximum between 1700 and 1400 cm^{-1} which spans the region normally associated with a range of carbonate type species (11) and indicates a considerable buildup of carbonates, principally on the Al_2O_3, under the reaction conditions.

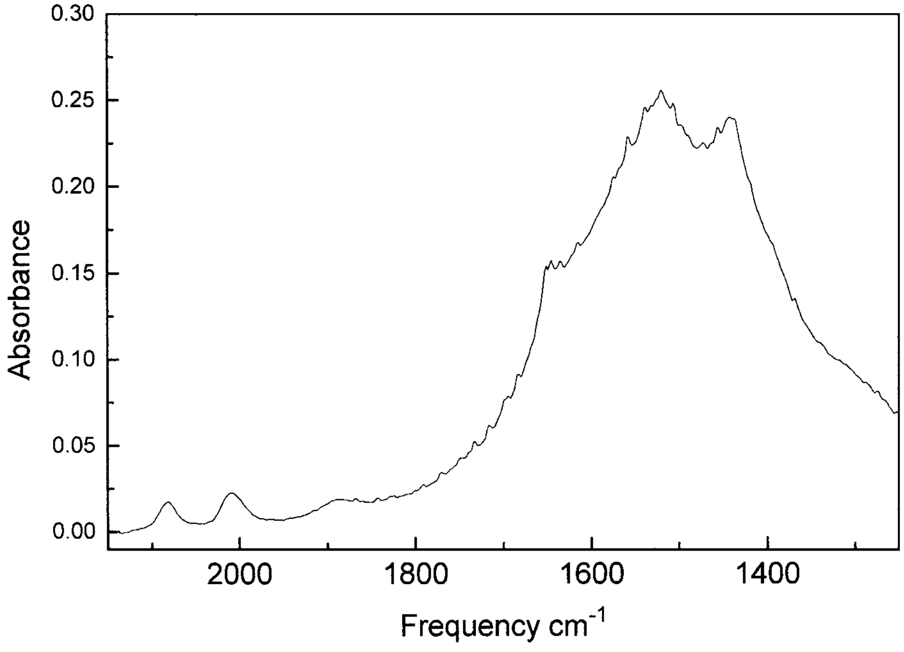

FIG. 1. DRIFTS spectrum after equilibration of the sample under the reaction mixture (5%CO, 3%O_2 in He at a total flow rate of 65 sccm) at 567 K.

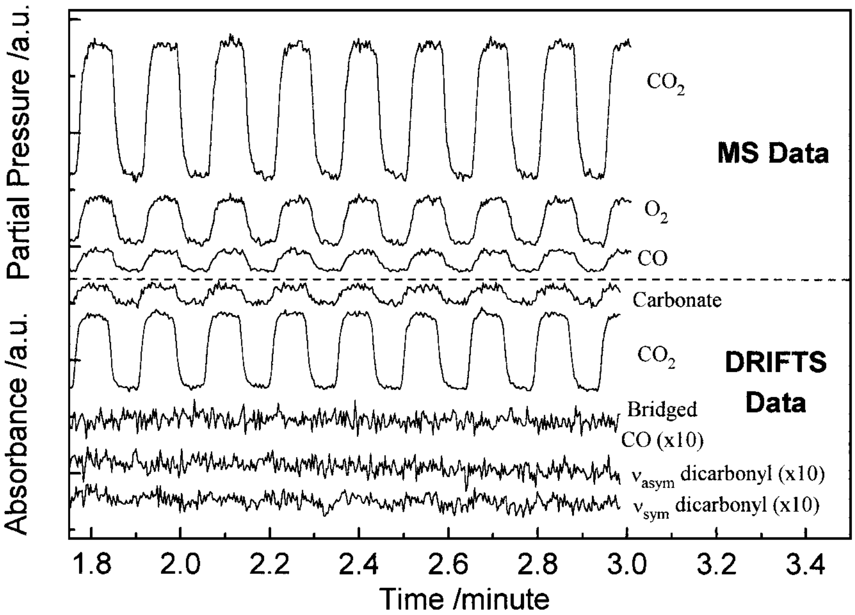

FIG. 2. Collected MS and DRIFTS trend analysis during modulation of the inlet reactant concentration at 0.11 Hz.

During modulation, the MS allowed the variation of the gaseous concentrations of CO, O_2, and CO_2 to be followed while integration of peak areas across a series of DRIFTS spectra enabled a similar trend analysis. Integration between 2433 and 2222 cm^{-1} again gave a measurement of the variation in gaseous CO_2 concentration and proved useful for synchronization of the MS and DRIFTS data while measurement between 2123 and 2047 cm^{-1}, 2047 and 1945 cm^{-1}, 1915 and 1820 cm^{-1}, and 1772 and 1580 cm^{-1} allowed the changes in intensity of the asymmetric and symmetric υ_{CO} of the gem-dicarbonyl species, bridged CO, and the surface carbonate, respectively, to be followed. The collected MS and DRIFTS traces from a period of 10 modulation cycles are shown in Fig. 2. Under the stated conditions, the gas phase concentrations of CO, O_2, and CO_2 all modulate approximately in phase with the rate of CO_2 production stepping between 25 and 11 μmol $m^{-2} s^{-1}$. Of the surface species, only the carbonates show a clear modulation in near perfect phase with the CO_2, CO, and O_2. Both traces associated with the dicarbonyl species show a gradual drop in absorbance with time. For these features, periodicity at the modulation frequency is much less evident than in any of the other traces with only the higher frequency symmetric dicarbonyl mode showing a slight variation in reasonable phase with the others. The negligible shift in phase between all traces indicates that the kinetics of the elementary reaction steps are, under the conditions employed, rapid with respect to the input modulation frequency.

The two spectra in the main body of Fig. 3 have each been produced by the coaddition of 40 individual spectra extracted from points corresponding to maximum and minimum rates in the DRIFTS data from four modulation cycles. Coaddition over only four cycles is ample to produce adequate signal to noise in this instance. The bands in Fig. 3 again correspond to gas phase CO_2, geminal dicarbonyl and various carbonate type species; however, intensity in this figure now represents a difference in absorbance with respect to the steady state. Thus positive and negative gas phase CO_2 peaks are visible, corresponding to the maximum and minimum conversion of CO_2 with the normal gas phase band envelope showing distortion due to an underlying peak from physisorbed CO_2. It is also clear that the reaction rate modulation is causing substantial changes in the carbonate region of the spectrum with features at 1649 and 1435 cm^{-1}, most likely associated with bicarbonate on the alumina (11, 12), appearing particularly labile.

On first inspection, the CO region of the spectra shows only small and consistently negative geminal dicarbonyl features. Their presence is in line with the slow leaching of the intensity from the peaks associated with the dicarbonyl species noted in Fig. 1 and identifies a slight drift in average inlet concentration between acquisition of the steady-state background and the modulation spectra. There does, however, seem to be some consistent deviation between maximum and minimum rate spectra at the high frequency side of the symmetric dicarbonyl peak at around 2100 cm^{-1}. To resolve this feature, the spectra in Fig. 3 have been subtracted from one another and the result in the region for adsorbed CO is shown in the insert. There is one well resolved peak at 2100 cm^{-1} on an otherwise flat baseline. This peak position corresponds well with the literature values of 2080–2100 cm^{-1} (14) and 2103 cm^{-1} (15) for CO on

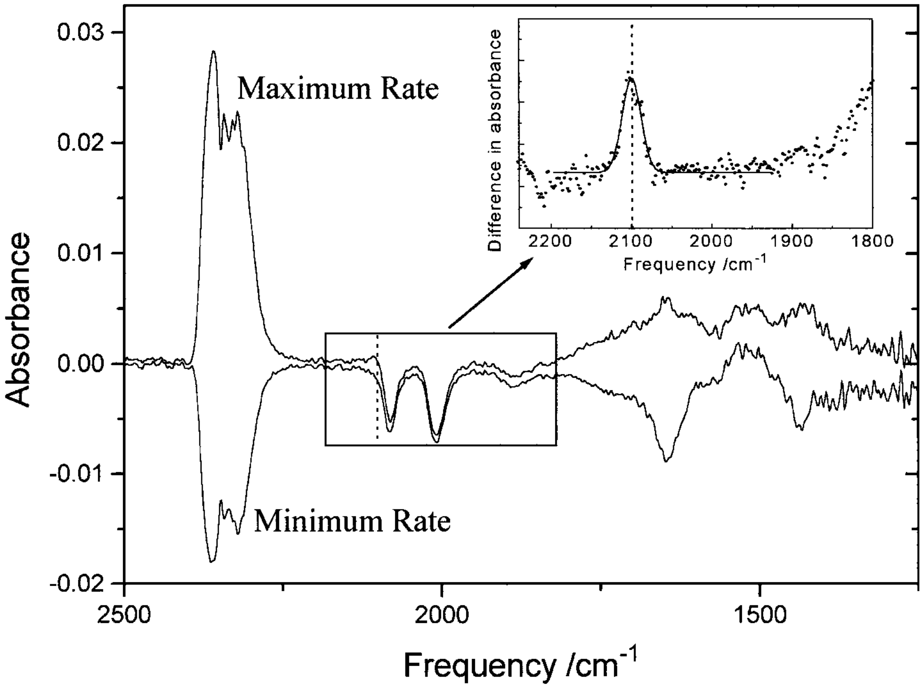

FIG. 3. DRIFTS spectra, each produced from coaddition of 40 individual spectra collected during maxima and minima in the modulation cycle. The inset shows the result of subtraction of the two spectra in the region for forms of adsorbed CO. The vertical dotted lines are at the maximum of the band in the inset (2100 cm^{-1}).

oxidized rhodium(I) sites. In this difference spectrum, the intensity of the peak is related to the differential conversion and clearly demonstrates that the geminal dicarbonyl species is a spectator to the reaction and the active species is CO on oxidized Rh. The inactivity of geminal dicarbonyl species has been demonstrated previously (16) but CO on Rh(I–III) sites has also been thought to be quite inactive with linear CO considered to be the active species (15). Although linear CO was briefly observed on the sample during the heating ramp (at 538–558 K) it is absent under the conditions used in the generation of these spectra. Were linear CO responsible for the activity it would be discovered by the subtraction technique used above and there would be a band in the inset in Fig. 3 at ~2050 cm^{-1}. Bridged CO is also absent from this spectrum and is thus inactive. There is no evidence above 2110 cm^{-1} for the existence of CO on more strongly oxidized Rh(II–III) sites (14) in any spectra, either conventional or difference.

CONCLUSION

Use of concentration modulation during *in situ* DRIFTS has been shown to be capable of producing spectra of the active species for CO oxidation on Rh/Al_2O_3 under conditions where its detection would be otherwise impossible due to overlapping bands from coadsorbed inactive spectator species. The active CO species has been shown to be CO on oxidized Rh sites rather than geminal dicarbonyl or linear CO on Rh metal. These experiments may be regarded as preliminary to full frequency response measurements where the dependence of the gas and surface concentration of species on modulation frequency should allow the exploration of the kinetics of adsorption, desorption, and surface reaction by application of frequency response techniques.

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