An *In Situ* IR Study Coupled with Transient Kinetic Analysis of Hydroformylation

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In situ infrared (IR) spectroscopy has been considered one of the most important means of studying reactive intermediates on supported catalysts. Most of the work was done at subatmospheric pressures and high temperatures (Yates et al., 1979; Worley et al., 1983). Several developments in *in situ* IR reactor cells (Hicks and Bell, 1981; Arakawa et al., 1986; Edwards and Schrader, 1981) have allowed catalytic reactions to be studied under high pressure and temperature conditions. This technique permits observation of absorbed species during reaction conditions. Distinguishing reactive adsorbed species from spectator species that do not participate in the reaction has been a major challenge in the fundamental research of heterogeneous catalysis (Tamaru, 1991). Steady-state isotopic transient kinetic analysis (SSITKA) has been developed to determine the surface coverage of reaction intermediates for CO hydrogenation and partial oxidation of methane, and the rate constants for the elementary steps (Biloen et al., 1983; Happel et al., 1980; Piel et al., 1989).

Combination of *in situ* IR technique with SSITKA will not only provide information for the determination of surface coverages of adsorbed species and the rate constants for elementary reactions, but also permit distinction between reactive adsorbed species and spectator species during the reaction. The objective of this study is to develop an *in situ* IR technique coupled with steady-state isotopic transient kinetic analysis for studying heterogeneous hydroformylation.

Experimental Technique

The catalyst used in this study was Rh-Ce/SiO_2 (atomic ratio of Rh:Ce = 1:1 containing 5 wt. % Rh), prepared by coimpregnating a solution of $RhCl_3 \cdot 3H_2O$ (Alfa) and $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa) onto a silica support (Strem). An *in situ* infrared reactor cell, capable of operating up to 513 K and 6 MPa, has been constructed for hydroformylation, and a detailed schematic of the reactor is given elsewhere (Chuang and Pien, 1992). An inlet system, shown in Figure 1, for switching ^{12}CO to ^{13}CO was designed to create a step change in the concentration of a steady-state reactant flow from Ar/CO, H_2, C_2H_4 (0.02:1:5:5) to ^{13}CO, H_2, C_2H_4 (1:5:5). The normal ratio of CO:H_2:C_2H_4 used in hydroformylation is 1:1:1, but the 1:5:5 ratio was used here to enhance the formation of the aldehyde under reaction conditions. Ar, an inert gas, is used with CO to determine the flow pattern through the reactor and transportation lines. It should be noted that the total reactant flow through the reactor was maintained constant throughout the experiment. Since ^{13}CO has the same chemical properties as ^{12}CO, a step change in the concentration from ^{12}CO to ^{13}CO would not perturb the chemical environment and the total surface concentration of adsorbed species during the reaction. The change in the concentration of the adsorbed species containing ^{12}C and ^{13}C during the switch was monitored by *in situ* IR spectroscopy using a Nicolet 5SXC FT-IR spectrometer with a resolution of 4 cm^{-1}. The effluent composition from the IR reactor cell was monitored continuously by a Balzers QMG 112 quadrupole mass spectrometer. The transient IR spectra were recorded every 3 s, and the mass spectroscopy data were collected at an interval of 0.3 s for each species. The composition of the products was determined by an HP 5890A gas chromatograph equipped with an FID.

Transient Response of Adsorbed Species and Gaseous Products

The amount of surface Rh was measured to be 28.5 μmol/g, by pulse CO chemisorption at 303 K, assuming the ratio of adsorbed CO to the surface Rh atom, CO_a/Rh = 1 (Konishi et al., 1987). Ethylene hydroformylation over Rh-Ce/SiO_2 catalyst at 453 K and 0.1 MPa produced C_2H_6 as the major species, and C_2H_5CHO and CH_4 as minor species, with turnover frequency (TOF) for propionaldehyde production of 0.43 min^{-1}. Figure 2 shows the response of the effluent composition determined by the mass spectrometer. Responses of $m/e = 29$ corresponding to ^{13}CO, $m/e = 59$ corresponding to $C_2H_5{}^{13}CHO$, and $m/e = 40$ corresponding to Ar, which were not affected by the fragmentation of other parent species, are shown in Figure 2. All the curves have been normalized to $F(t)$, which is the fraction of the final response, for comparison. Proper

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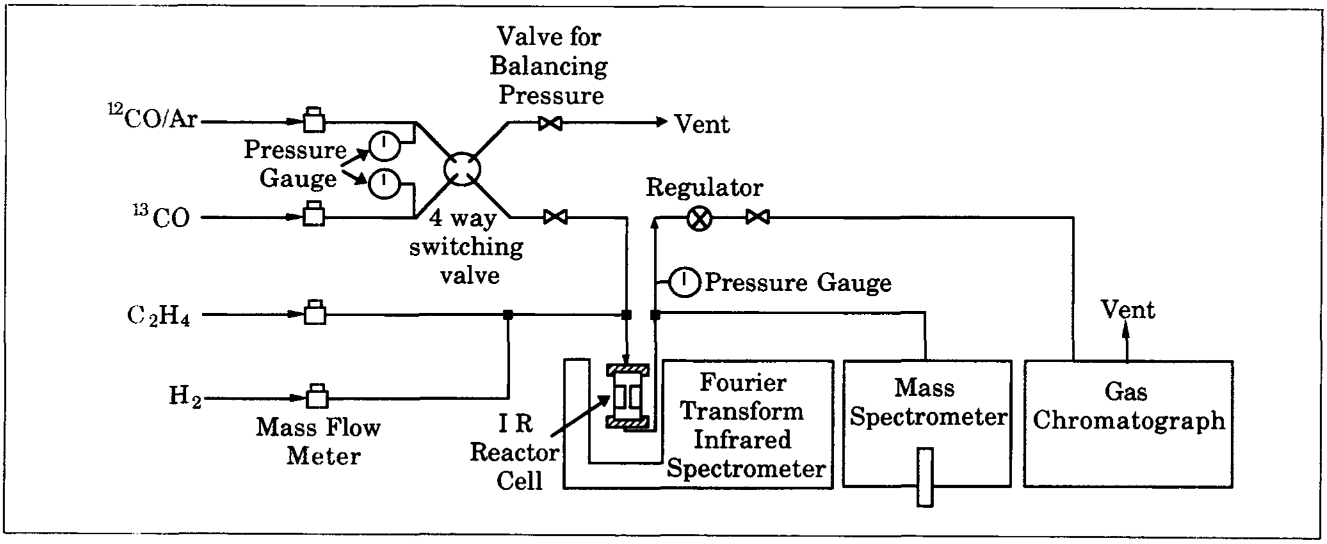

Figure 1. Combined *in situ* IR and M.S. system.

balancing of pressure and flow rates of the ^{12}CO/Ar mixture and ^{13}CO during the switch is essential for maintaining steady-state conditions. The evolution of ^{13}CO curve is faster than that of $C_2H_5{}^{13}CHO$. The completed switch from ^{12}CO to ^{13}CO was achieved at approximately 0.85 min, while the switch from C_2H_5CHO to $C_2H_5{}^{13}CHO$ took approximately 1.6 min.

Figure 3 shows the *in situ* IR spectra of the adsorbed species during the isotopic switch. Prior to the switch, the linear CO band at 2,027 cm^{-1}, bridge CO band at 1,864 cm^{-1}, a tilted CO band at 1,688 cm^{-1} (Underwood and Bell, 1988), a surface carbonate species at 1,543 cm^{-1} (Lavalley et al., 1990), and an ethylene band at 1,467 cm^{-1} were observed. Switching from ^{12}CO to ^{13}CO produced a shift in the linear CO band from 2,027 to 1,975 cm^{-1}, the bridge CO band from 1,864 to 1,837 cm^{-1}, and the tilted CO band from 1,688 to 1,657 cm^{-1}. To determine the changes in the IR spectra during the switch, difference spectra shown in Figure 4 were obtained by subtracting the spectrum at $t=0$ from the consecutive transient spectra. It should be noted that the low signal-to-noise ratio is due to the single spectrum collected without coaddition to facilitate rapid scanning.

Increase in both the negative feature at 2,027 cm^{-1} and positive feature at 1,975 cm^{-1} bands in the difference spectra indicates that the linear ^{12}CO is replaced by linear ^{13}CO. The displacement process was completed within 0.85 min for the linear CO, which correlates to the time for complete switching of the gaseous ^{13}CO response obtained from the mass spectrometer. The switching of tilted ^{12}CO at 1,688 cm^{-1} to tilted ^{13}CO at 1,657 cm^{-1} started at 0.18 min after commencement of the switch and was completed at 0.53 min, which was before the complete switching of linear CO. The reason for the slow start and rapid completion of the tilted CO remains to be

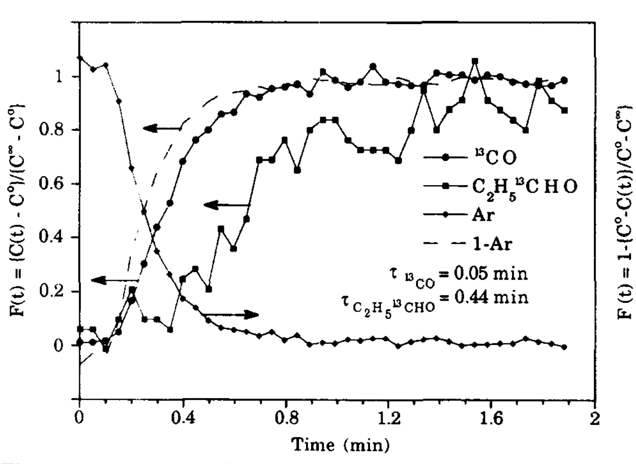

Figure 2. Fractional response of gaseous effluent species during isotopic switching from Ar/^{12}CO/H_2/C_2H_4 to $^{13}CO/H_2/C_2H_4$.

C^0 = steady-state concentration of the species before the switch
C^∞ = steady-steady concentration of the species after the switch
CO chemisorption = 28.5 μmol CO/g catalyst

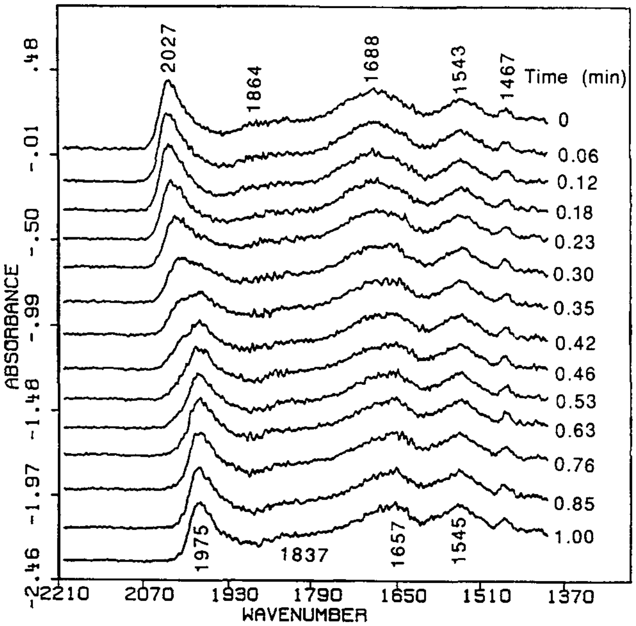

Figure 3. Transient infrared spectra of the surface species during isotopic switching from Ar/^{12}CO/H_2/C_2H_4 to $^{13}CO/H_2/C_2H_4$.

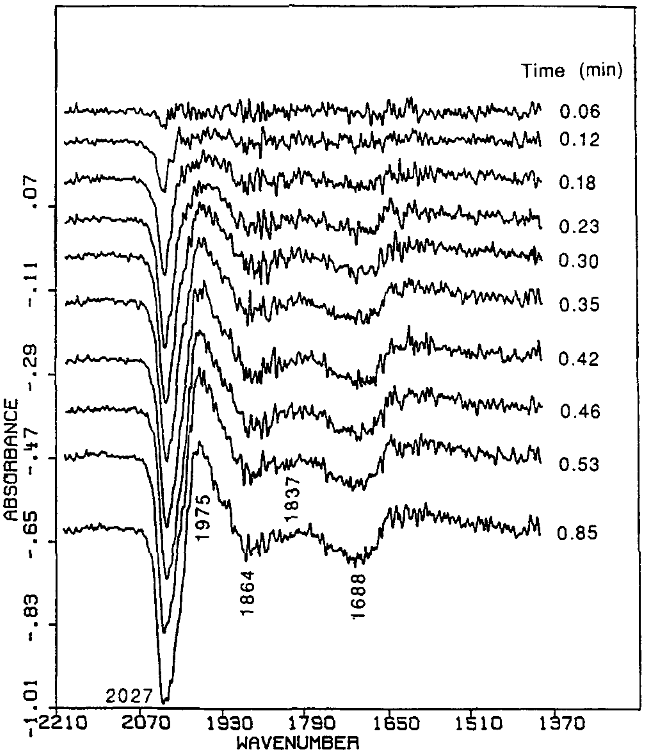

Figure 4. Difference spectra of Figure 3 obtained by subtracting spectrum at 0 min from each transient spectrum.

investigated. Little change in the difference spectra between 1,500-1,600 cm^{-1} indicates that the surface carbonate species exhibiting the 1,543 cm^{-1} band is a spectator species that does not participate in the catalytic reaction cycle.

Residence times, τ (min), for adsorbed CO species can be estimated by the area between the inverted normalized Ar curve and the ^{13}CO response curve (Biloen, 1983). Due to rapid exchange between the gas-phase CO and adsorbed CO, the gas-phase ^{13}CO response closely resembles that of linear ^{13}CO which has been identified as the precursor for CO insertion (Chuang and Pien, 1992). The residence time for the linearly adsorbed ^{13}CO species determined from the ^{13}CO response curve is 0.05 min. Similarly, the residence time for intermediates leading to $C_2H_5{}^{13}CHO$ is determined to be 0.44 min for the reaction, $^{13}CO_{(g)} \rightleftharpoons {}^{13}CO_{ads} \xrightarrow{C_2H_4/H_2} C_2H_5{}^{13}CO_{ads} \xrightarrow{H_{ads}} C_2H_5{}^{13}CHO$. $\theta_{C_2H_5CO}$ (moles of C_2H_5CO/moles of surface Rh) could be determined from $TOF = k\theta = \theta/\tau$ where k (min^{-1}) is the rate constant. $\theta_{C_2H_5CO}$ is found to be 0.19 using the above equation.

In conclusion, the IR method can provide structure of the adsorbed species; SSITKA can offer the surface coverage and rate constants for the elementary steps. Combination of the two techniques provides valuable information for distinction of spectator species from all IR observable species.

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