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## NOTE

# Transient Infrared Study of Methanation and Ethylene Hydroformylation over Rh/SiO₂ Catalysts

Determination of reactivity and surface coverage of intermediates has been a challenging goal in fundamental research of heterogeneous catalysis. First Happel *et al.* (*1*) and later Biloen and co-workers (*2, 3*) employed the use of a transient rate tracer method for the determination of the intrinsic rate constant, $k$, and the fractional surface coverage, $\Theta$, of intermediates for steady-state carbon monoxide hydrogenation. The method was further developed and termed steady-state isotopic transient kinetic analysis (SSITKA) by Goodwin and co-workers (*4, 5*). SSITKA is a transient method for the investigation of kinetics and mechanism of heterogeneous catalysis under steady-state conditions. The approach involves an abrupt switch from an inlet reactant species to a corresponding isotopically labeled species. The advantage of SSITKA from other transient methods is that the chemical environment of the catalyst surface does not vary with the transient state of the isotopic tracer, yielding tracer response curves for the determination of $k$ and $\Theta$ (*6, 7*). The method has been applied in the investigation of the mechanism of methanation (*1, 2, 8*), Fischer–Tropsch synthesis (*3, 9, 10*), ammonia synthesis (*5*), and partial oxidation of methane (*4*).

*In situ* infrared spectroscopy (IR) allows for the direct observation of adsorbed species under reaction conditions (*11*). Incorporation of *in situ* IR spectroscopy with SSITKA may provide information on the surface coverages of IR observable species under reaction conditions (*12*) and has the potential for distinguishing between reaction intermediates and surface adsorbed spectator species. This paper reports the use of IR combined with SSITKA to study methanation and ethylene hydroformylation on $Rh/SiO_2$ at 513 K and 0.1 MPa.

The 3 wt% $Rh/SiO_2$ catalyst was prepared by the incipient wetness method. An aqueous solution of $Rh(NO_3)_3 \cdot 2H_2O$ (Johnson–Matthey) was impregnated into a $SiO_2$ support (Strem Chemicals). The ratio of solution and silica support was 1 : 1. After impregnation, the sample was dried overnight in air at 301 K and then reduced in flowing $H_2$ at 673 K for 16 h. The $H_2$ uptake of the catalyst at room temperature was measured to be 29.0 μmol/g. Details of the catalyst characterization have been reported elsewhere (*13*). Sixty-three mg of the catalyst was pressed into self-supporting disks and placed in an IR reactor cell which has a void volume of 0.64 cm$^3$. The IR reactor cell acts like a differential reactor. The catalyst was further reduced at 513 K for 2 h *in situ* before each experiment.

The flowrates of CO, $H_2$, and He were 10, 10, and 20 cm$^3$/min, respectively, during CO hydrogenation, and the flowrates of CO, $H_2$, and $C_2H_4$ were 20, 20, and 20 cm$^3$/min, respectively, for hydroformylation. Both reactions were held at steady-state for 1 h before the isotopic switch. The CO contains 2% Ar for determining the effect of gas-phase holdup in the reactor and the gas transportation lines on the transient response of gaseous products. The average residence time of the Ar response is the sum of the average residence times of the reactant flow in the transportation lines, the reactor, and the MS inlet system. The switch between CO ($^{12}CO$) and $^{13}CO$ is made via a low-dead-volume Valco switch valve. The IR spectra were recorded by a

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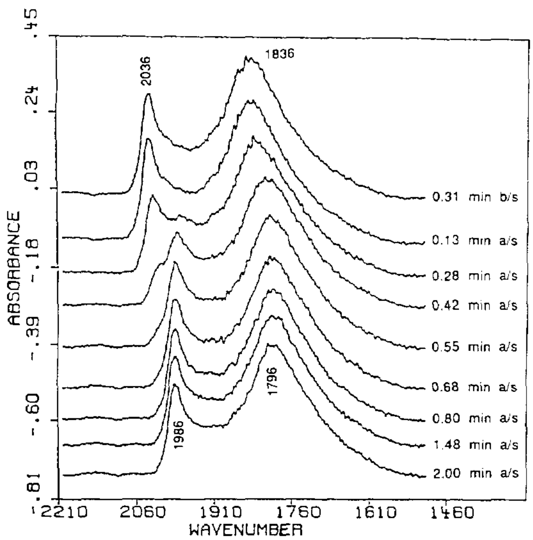


FIG. 1. The *in situ* infrared spectrum of methanation during the isotopic transient switch between CO and $^{13}CO$; b/s denotes before switch, a/s denotes after switch.

Nicolet 5SXC spectrometer with a DTGS detector at a resolution of 4 $cm^{-1}$ and a rate of 1 scan per s. For a low signal-to-noise ratio, three scans were coadded for the transient data. The transient response of the gaseous products from the IR cell were recorded by a Balzers QMG112 mass spectrometer (MS) interfaced to a microcomputer. The MS is equipped with a differentially pumped inlet system for fast response. The *m/e* ratios followed by the MS were 15 for $CH_4$, 28 for CO, 29 for $^{13}CO$, 40 for Ar, and 59 for $C_2H_5{}^{13}CHO$. The *m/e* ratios were carefully selected to prevent interference from the fragmentation of parent species. The gaseous products were analyzed by a HP-5890A gas chromatograph with an FID detector.

Methane was the only hydrocarbon product observed during CO hydrogenation over $Rh/SiO_2$ at 513 K and 0.1 MPa with a turnover frequency (TOF) of 0.015 $min^{-1}$. The TOF reported here agrees with that reported elsewhere for $Rh/SiO_2$ (*14*). The conversion of CO was 0.01%. Figure 1 is the IR transient response to an isotopic switch from CO to $^{13}CO$ during CO hydrogenation. The IR spectra for CO hydrogenation before the switch shows a linearly adsorbed CO band at 2036 $cm^{-1}$ and a bridge adsorbed CO band at 1836 $cm^{-1}$. A step decrease in the CO inlet concentration with a simultaneous increase in the inlet $^{13}CO$ concentration caused the linear and bridged CO to be replaced by linear and bridged $^{13}CO$ at the same rate. The replacement is complete at 0.68 min after the switch.

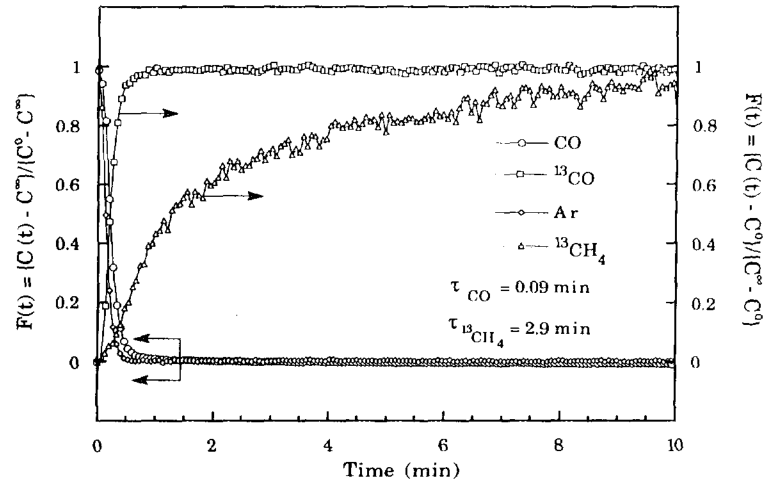


FIG. 2. Fractional tracer response of the gaseous products to the switch from CO to $^{13}CO$ during methanation. $C^0$ = initial concentration; $C^\infty$ = final concentration.

The gas-phase product response to the isotopic switch is shown in Fig. 2. The transient curves have been normalized to $F(t)$, the fraction of the final response, for comparison. The CO and $^{13}$CO curves are shown to illustrate the switch between the two chemically equivalent gases. The CO curve lags behind the Ar curve because of the occurrence of adsorption and desorption of CO that did not react toward the product $CH_4$. The fraction of adsorbed CO which desorbs without further reaction to the total surface exposed Rh determined from the area between the CO and the Ar response was 0.67. The time for the complete replacement of the gaseous CO by $^{13}$CO measured by mass spectroscopy agrees very well with that of the adsorbed CO replacement measured by IR spectroscopy. This is direct evidence showing that the adsorption of CO on $Rh/SiO_2$ is a rapid, reversible process under reaction conditions. The $^{13}CH_4$ response curve is much slower than the Ar and $^{13}$CO response curves. Integration of the normalized transient curve provides the average residence time for the measured response (*15*). The actual residence time of the transient intermediates leading to gaseous species can be calculated by subtracting the residence time of the Ar response from the residence time of the labeled species. The average residence time for the intermediates involved in the formation of methane, $\tau_{CH_4}$, was determined to be 2.9 min. With the measured value of TOF and $\tau$, the surface coverage, coverage, $\Theta$, of intermediate species can be calculated from the equation

$$\mathrm{TOF} = k\Theta = (1/\tau)\Theta, \qquad (1)$$

assuming that the formation of $CH_4$ from adsorbed CO is an irreversible step. The fractional surface coverage as calculated from Eq. (1) is an upper limit to the actual surface coverage of $CH_x$ species because it incorporates all surface carbon-containing species that react irreversibly toward $CH_4$ (*2*). The fractional surface coverage, $\Theta_{CH_x}$, is calculated to be 0.043 for methanation. The measured surface coverage of adsorbed CO and $CH_x$ is the same order of magnitude to those reported for $Rh/Al_2O_3$ (*8*) at 493 K ($H_2$ : CO = 9 : 1) and $Rh/SiO_2$ (*14*, *16*) at 526 K ($H_2$ : CO = 3 : 1) and 483 K ($H_2$ : CO = 2 : 1), respectively.

The product distribution for the reaction of ethylene with syngas at 513 K and 0.1 MPa contained $C_1$–$C_4$ hydrocarbons and $C_2H_5CHO$, the product of hydroformyla-

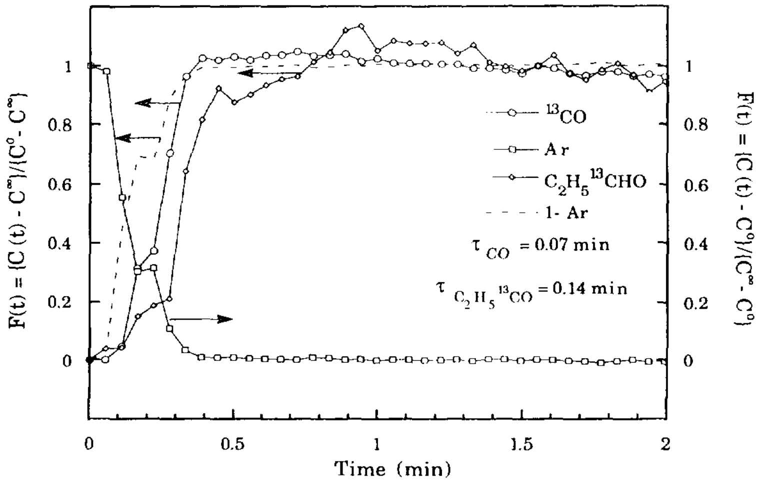
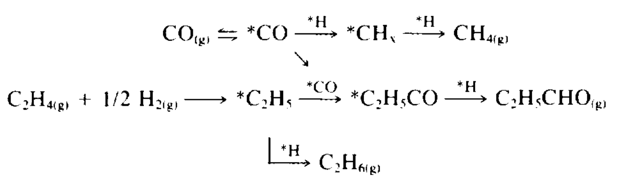


FIG. 3. Fractional tracer response of the gaseous products to the switch from CO to $^{13}$CO during hydroformylation. $C^0$ = initial concentration; $C^\infty$ = final concentration.

tion. The TOF of $C_2H_5CHO$ was measured to be 0.13 min$^{-1}$. The conversion of CO was 0.11%. The IR spectra of the isotopic switch during hydroformylation is very similar to that of methanation. No IR bands for the adsorbed product were observed, indicating rapid desorption of the product. A linear CO band at 2037 cm$^{-1}$ and a bridge CO band at 1842 cm$^{-1}$ are rapidly replaced with $^{13}CO$ bands at 1986 and 1797 cm$^{-1}$, respectively. Figure 3 is the normalized gaseous product response of the isotopic switch at 513 K and 0.1 MPa for the ethylene hydroformylation reaction. Shown in the figure are the responses of Ar, $^{13}CO$, and $C_2H_5{}^{13}CHO$. The rate of appearance of $^{13}CO$ in the gas phase is in good agreement with that of the appearance of adsorbed $^{13}CO$ on the surface of the catalyst. From the $^{13}CO$ and the Ar response, the surface coverage of CO was calculated to be 0.57. The decreased CO coverage as compared to methanation is due to the presence of ethylene during hydroformylation. The residence time for intermediates involved in propionaldehyde formation, $\tau_{C_2H_5CHO}$, was determined to be 0.14 min. Using Eq. (1), the upper limit to the fractional surface coverage for carbon-containing species that irreversibly react to propionaldehyde is calculated to be 0.018.

The proposed reaction scheme (*17–19*) for the methanation and hydroformylation can be summarized in the following:



$$CO_{(g)} \rightleftharpoons {}^*CO \xrightarrow{*H} {}^*CH_x \xrightarrow{*H} CH_{4(g)}$$

$$C_2H_{4(g)} + 1/2\ H_{2(g)} \longrightarrow {}^*C_2H_5 \xrightarrow{*CO} {}^*C_2H_5CO \xrightarrow{*H} C_2H_5CHO_{(g)}$$

$$\xrightarrow{*H} C_2H_{6(g)}$$

Here * indicates adsorbed sites. During the methanation reaction, adsorbed CO can dissociate and then hydrogenate to produce methane. The addition of ethylene to syngas initiates the formation of ethane and propionaldehyde. The effect of added ethylene on the transient response of $CH_4$ remains to be investigated. Propionaldehyde is formed by the insertion of linearly adsorbed CO into the adsorbed $^*C_2H_5$ species which is generated from the hydrogenation of ethylene (*13*). A short residence time reflects high reactivity of intermediates, which corresponds to a large intrinsic rate constant. The results of this study indicate that the reaction sequence involving CO insertion and subsequent hydrogenation leading to $C_{2+}$ oxygenates is much faster than CO dissociation followed by hydrogenation resulting in hydrocarbons. A higher rate constant of CO insertion compared to that of the formation of methane on $Rh/SiO_2$ has also been noted by Jackson *et al.* (*20*) in transient pulse experiments. Further modeling will be required to determine the intrinsic rate constants for elementary steps and the surface coverage of various intermediates involved in the catalytic reaction.

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