Quantitative FTIR Determination of Extinction Coefficients of Adsorbed CO

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A combined IR and MS technique was used to determine extinction coefficients of adsorbed CO on the 4% Rh/SiO_2 catalyst. An isotopic exchange experiment has been made to obtain accurate integrated absorption intensities. The experimental procedure provides a fast and accurate, as well as a highly reproducible, method for the determination of extinction coefficients of adsorbed surface species. Integrated absorption intensities for $Rh^+(^{12}CO)$ and $Rh^+(^{13}CO)_2$ were determined at 373 K and 0.1 MPa to be 1.35 and 8.02 cm/μmol, respectively.

Introduction

In situ Fourier transform infrared spectroscopy (FTIR) has been one of the most important means of studying IR-observable adsorbates on supported metal catalysts under reaction conditions (Yang and Garland, 1957; Arai and Tominaga, 1976; Srinivas *et al.*, 1994; Chuang *et al.*, 1995a; Krishnamurthy *et al.*, 1995). Although FTIR is most often thought of as a qualitative tool useful in identifying species present during surface reactions, it can also be used, under certain circumstances, as a means of determining surface concentration. For example, quantitative IR spectroscopy has been used to determine metal dispersion and the number of surface sites (Rasband and Hecker, 1993). During propylene hydroformylation on Rh/SiO_2, Srinivas and Chuang (1993) have used quantitative IR spectroscopy to estimate the number of Rh surface atoms required for determination of the turnover number frequency (TOF). Other examples of applied quantitative FTIR for chemisorbed CO can also be found in recent literature (Winslow and Bell, 1984; Kaul and Wolf, 1984; Yokomizo *et al.*, 1989).

The relation most often used to relate the CO surface concentration to IR peak areas is the integrated Beer−Lambert relation (Rasband and Hecker, 1993):

$$a_i = A_i l c_i \tag{1}$$

where a_i is the area under the IR absorbance peak attributed to species i, l is the sample thickness, and c_i is the concentration of i. A_i is the integrated absorption intensity which can also be thought of as an extinction coefficient for i. Cavanagh and Yates (1981) have concluded that the *gem*-dicarbonyl CO [$Rh^+(CO)_2$] adsorption intensity was essentially independent of the coverage for a 0.2% Rh/Al_2O_3 catalyst; Rasband and Hecker (1993) have shown that extinction coefficients or integrated absorption intensities for linear and bridged CO vary little over the temperature range of 323−473 K as well as for average spherical particle diameters ranging from 13 Å to 58 Å (100 to 22% dispersion). These discoveries broaden the application of quantitative FTIR so that the extinction coefficient determined for one temperature, metal dispersion, and coverage may be used for other temperatures, dispersions, and coverages. Qualitative FTIR has been and continues to be one of the most utilized tools in the characterization of support metal catalysts; quantitative FTIR has the potential to allow determination of the surface concentration of active intermediates in catalytic reactions. The objective of this work is to report additional extinction coefficient data for adsorbed CO which were determined by a combined infrared spectroscopy (IR) and mass spectrometry (MS) technique. A knowledge of the extinction coefficients allows the quantitative determination of the concentrations of surface adsorbed species using FTIR.

Experimental Section

A schematic of the apparatus appears in Figure 1. The apparatus has been described in detail by Chuang *et al.* (1995a). The gas inlet section is designed to deliver gases to the IR reactor cell. The flow rates of the gases are controlled by Brooks 5850 Series E mass flow controllers. Pulse injection of the reactant mixture into an inert carrier flow can be achieved with a six-port sampling valve. The IR cell consists of a central stainless steel hollow cylinder with 3-mm-thick walls and two flanges welded to both ends. The catalyst sample for the transmission IR study is pressed in the form of a thin disk and is placed in the center of the cylinder sealed with CaF_2 rod windows. CaF_2 rods polished on both ends are 55.5 mm in length and 10 mm in diameter. The CaF_2 windows, placed in a machined channel within each flange, are 25 mm in diameter and 5 mm in thickness. Both faces of the windows are pressed by flanges with Viton O-rings.

The analytical instrumentation includes an IR spectrometer to measure the adsorption intensity and vibrational frequency of the adsorbed species. The IR spectrometer is a Nicolet 5SXC with a DTGS detector. The resolution of the IR spectrometer is 4 cm^{-1}. The effluent from the IR reactor cell was originally fed to the mass spectrometer via a Nupro three-way cross-pattern fine metering valve and through capillary tubing (0.5 mm i.d.). The mass spectrometer (MS) is a Balzers QMG 112 quadrupole with an axial secondary electron multiplier. The time required to scan and record each mass-to charge (m/e) signal is less than 1 s. The m/e monitored by the MS were $m/e = 28$ for CO, $m/e = 29$ for ^{13}CO, $m/e = 44$ for CO_2, $m/e = 45$ for $^{13}CO_2$, and $m/e = 4$ for He.

Results and Discussion

Determination of integrated absorption intensities experimentally requires a way to independently measure the amount of each species i on the surface. An effective way to determine the amount of adsorbed CO on the catalyst surface has been developed. The following procedure was

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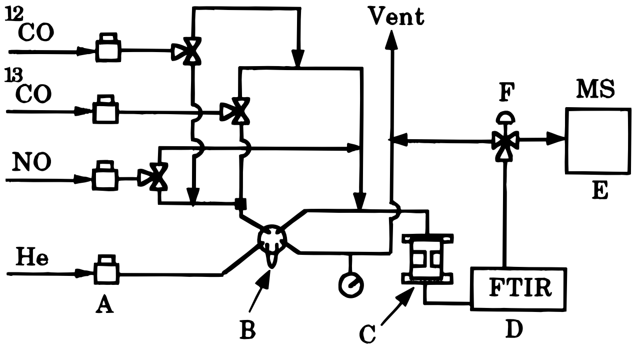

Figure 1. Apparatus: (A) Brooks 5850 Series E mass flow controllers, (B) six-port sampling valve, (C) *in situ* IR reactor cell, (D) Nicolet 5SXC IR spectrometer with DTGS detector, (E) Balzers QMG112 quadrupole mass spectrometer, (F) Nupro three-way cross pattern fine metering valve.

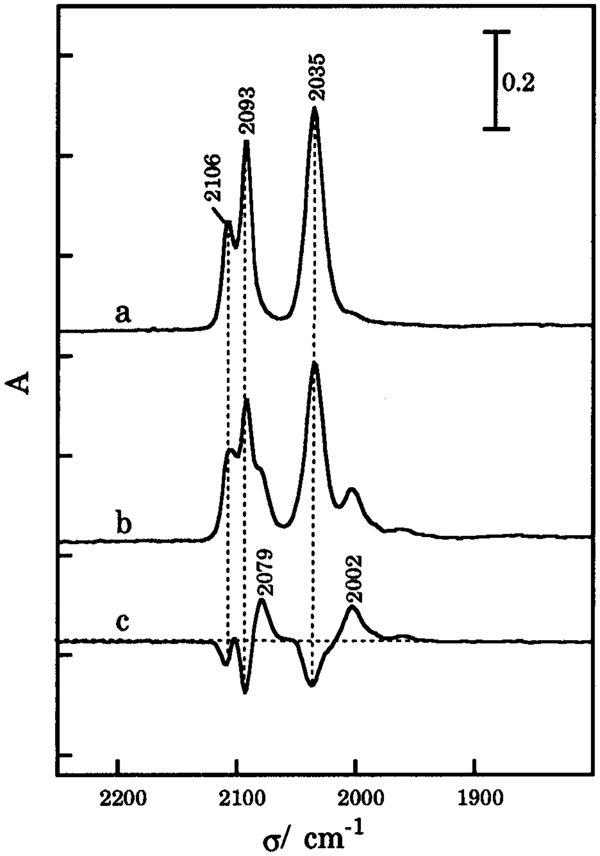

Figure 2. IR spectra of (a) adsorption of ^{12}CO on oxidized 4% Rh/SiO$_2$ at 373 K and 0.1 MPa, (b) pulse injection of 25 μL of ^{13}CO into 30 cm^3/min He at 373 K and 0.1 MPa on preadsorbed ^{12}CO, and (c) the difference spectrum of (b) − (a) as a function of wavenumber σ.

used to determine the extinction coefficients of CO present on the Rh/SiO$_2$ surface. Prior to the quantitative FTIR study, the 4% Rh/SiO$_2$ catalyst was first oxidized with air at 673 K for 1 h and then cooled down to 373 K in helium flow. Exposure of the oxidized catalyst to CO at 373 K and 0.1 MPa gives spectrum a in Figure 2. The IR band at 2106 cm^{-1} is attributed to linear ^{12}CO adsorbed on Rh$^+$ sites, Rh$^+$(^{12}CO). *gem*-Dicarbonyl ^{12}CO, Rh$^+$(^{12}CO)$_2$, exhibits the asymmetrical and symmetrical vibrational frequencies at 2093 and 2035 cm^{-1}, respectively. The assignment of the bands is consistent with the literature (Rice *et al.*, 1981; Chuang *et al.*, 1995b).

The bonding of CO to Rh involves formation of σ and π bonds. The donation of electrons from the slightly antibonding 5σ-orbital of CO into unfilled metal orbitals (Rh$^+$) strengthens the C−O bond and shifts the stretching vibration of adsorbed CO to a higher frequency, from about 2055 cm^{-1} (Rh^0−CO) to 2106 cm^{-1} (Rh$^+$(CO)). Donation of electrons from the filled metal *d*-orbitals into the vacant π^*-antibonding orbitals of CO weakens the C−O bond and shifts the stretching vibration frequency of CO to lower frequencies. The stretching vibration frequency of adsorbed CO thus depends on the relative contributions of the σ- and π-bonding.

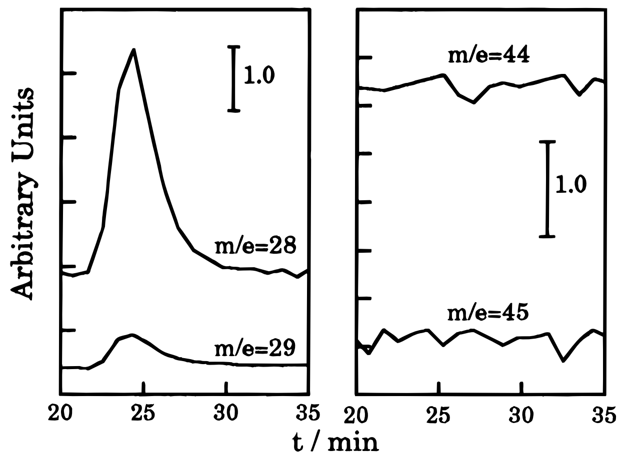

Figure 3. Corresponding MS response of IR reactor effluents to a 25 μL ^{13}CO pulse injection.

Spectrum b in Figure 2 is obtained after a pulse injection of 25 μL of ^{13}CO on the preadsorbed ^{12}CO. Pulsing, instead of flowing, the reactant to the IR reactor allows accurate mass balance calculation. The isotopic exchange between adsorbed ^{12}CO and gaseous ^{13}CO is evidenced by the emergence of Rh$^+$(^{13}CO)$_2$ bands at 2079 and 2002 cm^{-1} and the decrease in IR intensities of adsorbed ^{12}CO. The exchange can be clearly elaborated when spectrum a is subtracted from spectrum b, giving the difference spectrum c. Spectrum c clearly discerns the positive-peak areas, which correspond to Rh$^+$(^{13}CO)$_2$, and the negative-peak areas, corresponding to the desorption of Rh$^+$(^{12}CO) and Rh$^+$(^{12}CO)$_2$. The difference spectrum allows accurate integration of areas under the IR absorbance peaks. It is important to note that the replacement of Rh$^+$(^{12}CO) with Rh$^+$(^{13}CO) could have occurred. The band for Rh$^+$(^{13}CO) is in the region which is buried under the asymmetrical peak of Rh$^+$(^{12}CO) at 2093 cm^{-1}. However, the ratio of the areas of *gem*-dicarbonyl peaks in spectrum a is identical to the ratio of the negative areas due to *gem*-dicarbonyl in spectrum c, suggesting that the formation of Rh$^+$(^{13}CO)$_2$ is insignificant. Furthermore, the interaction and exchange between adsorbed ^{12}CO and gaseous ^{13}CO did not produce ^{12}CO$_2$ ($m/e = 44$) and ^{13}CO$_2$ ($m/e = 45$), as shown in Figure 3; thus, the amount of adsorbed ^{12}CO desorbed corresponds to the amount of CO ($m/e = 28$) in the reactor effluent. The amount of ^{13}CO adsorbed on the catalyst surface can also be obtained from the difference between the reactant effluents from the blank reactor and the reactor with the catalyst.

The MS response curves represent the change in concentration of each species monitored as a function of time. The m/e intensity $I_i(t)$ for each species can be converted to the rate of elution (F_i [=] μmol s^{-1}) by using

$$F_i = Cal_i I_i(t) \qquad (2)$$

where Cal_i, the calibration factor for species *i*, is determined by (Chuang *et al.*, 1995a)

$$N_o = Cal_i \int_0^t I_i(t)\,\mathrm{d}t \qquad (3)$$

N_o is the number of moles of the species injected in the calibration run. The unit for Cal_i is also in the number of moles. $\int_0^t I_i(t)\,\mathrm{d}t$ is obtained from the integration of the area under the response curve resulting from the pulse injection of a known amount of species i. The calibration factor is a function of ionizing current, vacuum in the ionization chamber, the pumping speed, and the flow rate of the carrier gas. The ratios of calibration factors are generally independent of the operating variables, thus only requiring a calibration pulse of a common ratioed species for each experimental run. Table 1 lists the ratios of calibration factors obtained prior to the reaction studies.

The infrared spectra and gaseous composition profile shown in Figures 2 and 3 permit the determination of the integrated absorbance coefficients for $Rh^+(^{12}CO)$, $Rh^+(^{12}CO)_2$, and $Rh^+(^{13}CO)_2$ by assuming that the integrated absorbance coefficients do not vary with the coverage of adsorbed CO and using the relation (Winslow and Bell, 1984)

$$\bar{A}_{CO} = \frac{1}{\bar{C}_{CO}} \int_{\nu_1}^{\nu_2} A(\nu)\,\mathrm{d}\nu \qquad (4)$$

where $\bar{C}_{CO}$ is the moles of CO chemisorbed per cross sectional area of the catalyst disk. $A(\nu)$ is the adsorbate's absorbance which is the function of wavenumber ν, and ν_2 and ν_1 are the upper and lower wavenumber bounds, respectively. The cross sectional area of the catalyst disk is measured to be 0.79 cm^2. It is noteworthy that the integrated absorption intensities determined from eq 4 are independent of the mass of the catalyst. The pulsing of 25 μL (1.01 μmol) of ^{13}CO into He carrier over 6.1 mg of the 4% Rh/SiO_2 catalyst at 373 K, spectrum b, desorbed 13.12 μL (0.53 μmol) of ^{12}CO and adsorbed 11.42 μL (0.46 μmol) of ^{13}CO. $\bar{A}_{CO}$ for $Rh^+(^{13}CO)$ is determined to be 8.02 cm/μmol.

The total amount of ^{12}CO desorbed is contributed by both $Rh^+(^{12}CO)$ and $Rh^+(^{12}CO)_2$. For this case, the mass balance can be written as

$$n_l + n_g = n_{tot} \qquad (5)$$

Equation 5 can be modified slightly to include the integrated absorption intensities and written as

$$\frac{a_l}{\bar{A}_l} + \frac{a_g}{\bar{A}_g} = n_{tot} \qquad (6)$$

where a_l and a_g are the areas under the IR absorbance peaks attributed to $Rh^+(^{12}CO)$ and $Rh^+(^{12}CO)_2$, respectively. Since n_{tot} is known (0.53 μmol) and a_l and a_g can be obtained from the FTIR spectrum, eq 6 provides one relation in the unknowns A_l and A_g. For this case, a_l and a_g are determined from the negative peaks in spectrum c of Figure 2 to be 0.43 cm^{-1} and 2.31 cm^{-1}, respectively. The integrated adsorption intensity for $Rh^+(^{12}CO)_2$ for this catalyst, A_g, was obtained from the recent study under the same condition to be 10.9 cm/μmol (Chuang *et al.*, 1995b). With this information, A_l is the only unknown in eq 6 and was determined to be 1.35 cm/μmol. Table 2 shows the integrated absorption intensities (extinction coefficients) for various adsorbed CO and NO on supported Rh catalysts which were obtained using the combined IR and MS technique. The differences in the values of the integrated coefficients for these chemisorbed CO may be due to the different character of the Rh sites and interactions between the dipoles of the CO molecule. Rh−CO (on Rh^0 sites) has an integrated coefficient lower than that of $Rh^+(CO)$ which is probably due to the weaker C−O bond in Rh−CO resulting from the donation of electrons from the filled Rh^0 metal d-orbitals into the vacant π*-antibonding orbitals of CO. The smaller value of the integrated absorption intensity of $Rh^+(CO)_2$ compared with that of Rh−CO may be attributed to the absence of a dipole−dipole interaction between the nearby C−O dipoles. The different extinction coefficients between $Rh^+(CO)$ and $Rh^+(CO)_2$ remain to be investigated.

Table 1. List of MS Calibration Factors

species i/species j	$(m/e)_i/(m/e)_j$	ratios of calibration factors	V/μL
$^{12}CO^-/^{13}CO^-$	(28)/(29)	1.48	500
CO^-/CO_2^-	(28)/(44)	1.33	500
CO_2/CO_2^{2-}	(44)/(22)	50.8	500
CO^-/NO^-	(28)/(30)	1.31	250
CO^-/N_2O^-	(28)/(44)	18.6	250
NO^-/N_2O^-	(30)/(44)	14.17	250
N_2^-/CO^-	(28)/(28)	0.082	25
N_2^-/NO^-	(28)/(30)	3.3	25
CO^-/NO^-	(28)/(30)	4.12	25

Table 2. Integrated Absorption Intensities for Various Adsorbed NO and CO Obtained Using the Combined IR and MS Technique

catalysts	surface adsorbed species (adsorbates)	integrated absorption intensity (cm/μmol)	ref
4% Rh/SiO_2	$Rh^+(^{12}CO)_2$	10.9	Chuang *et al.*, 1995b
4% Rh/SiO_2	$Rh-NO^-$	9.9	Krishnamurthy *et al.*, 1995
4% Rh/SiO_2	$Rh^+(CO)$	1.35	this work
4% Rh/SiO_2	$Rh^+(^{13}CO)_2$	8.02	this work
3% Rh/SiO_2	Rh−CO	35	Srinivas and Chuang, 1993
3% Rh/SiO_2	Rh_2CO	114	Srinivas and Chuang, 1993
3% S−Rh/SiO_2	Rh−CO	36	Srinivas and Chuang, 1993

Conclusions

Extinction coefficients of adsorbed CO on the 4% Rh/SiO_2 catalyst were determined by a combined IR and MS technique. An isotopic exchange experiment has been made to obtain the accurate integrated absorption intensities. The experimental procedure as described provides a fast, accurate, and highly reproducible method for the determination of extinction coefficients of adsorbed surface species. Integrated absorption intensities for $Rh^+(^{12}CO)$ and $Rh^+(^{13}CO)_2$ were determined at 373 K and 0.1 MPa to be 1.35 cm/μmol and 8.02 cm/μmol, respectively. The effect of isotopic exchange on the integrated absorbance intensity of *gem*-dicarbonyl was found to be insignificant.

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