Infrared Spectroscopic Observation of Intermediate Species on Ni and Fe Electrodes in the Electrochemical Reduction of CO_2 and CO to Hydrocarbons

Osamu Koga,* Tadanori Matsuo, Hiroki Yamazaki, and Yoshio Hori*

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi-cyo, 1-33, Inage-ku, Chiba 263

(Received July 23, 1997)

Adsorbed species on Ni and Fe electrodes were investigated by in-situ infrared spectroscopy in the electrochemical reduction of CO_2 or CO. Two types of adsorbed CO on the Ni electrode and one type on the Fe electrode were detected in a CO atmosphere. The two types, assigned to linear and bridged CO molecules, were also formed on the Ni electrode in CO_2 reduction. The negative polarization decreased the coverage of the adsorbed CO on Ni. The decay rate constants were evaluated from the spectroscopic data; the rate constant for the linear type was three times higher than that for the bridge one. Both constants agreed well with those determined from the formation rate of hydrocarbons in CO reduction, confirming that both adsorbed CO molecules were intermediate species to hydrocarbons. The high electrocatalytic activity of Cu in hydrocarbon formation from CO_2 and CO was rationalized in terms of the adsorption strength of CO on metals by comparing the activity of Ni, Fe, and Cu electrodes with the infrared bands of adsorbed CO on these electrodes. The weaker adsorption of CO on Cu led to higher activity.

CO_2 and CO can be electrochemically reduced to hydrocarbons and alcohols in aqueous media at a Cu electrode at high current densities.[1—5] A Ni electrode can also reduce CO_2 and CO to CH_4, C_2H_4, and C_2H_6 with a lower current efficiency.[6] Fe, which is not active in CO_2 reduction, can reduce CO to hydrocarbons.[7] It is thus interesting to reveal intermediate species on these electrodes in the electrochemical reduction of CO_2 and CO by an in-situ spectroscopic method.

A few papers have reported on the spectroscopic detection of intermediate species in the electroreduction of CO_2. A Pb electrode yields formate ion from CO_2.[1,5,8,9] Aylmer–Kelly et al. showed the formation of CO_2^- during a reaction on a Pb electrode.[10] Although Pt electrodes reduce CO_2 to "reduced CO_2", they actually yield hydrogen as the major product in the continuous electrochemical reduction of CO_2.[5,9] Beden et al. revealed by infrared spectroscopy that "reduced CO_2" at a platinum electrode in acidic solution is CO strongly bonded on the surface.[11] Iwasita et al. observed an absorption peak in a lower infrared region in the same system, and assigned it to the COH species.[12]

We previously demonstrated that adsorbed CO is an intermediate species in CO_2 rediction at Cu electrodes by electrochemical[13] and infrared spectroscopic methods.[14] During the electroreduction of CO_2 and CO in aqueous solutions, the Cu surface is practically saturated with adsorbed CO, which greatly prevents hydrogen evolution.

The hydrogen evolution is suppressed during the reduction of CO_2 or CO at Ni and Fe electrodes as well.[6,7] We presumed that adsorbed CO is formed as an intermediate species on the Ni electrode surface. We confirmed this hypothesis and preliminarily reported on the spectroscopic detection of adsorbed CO on an Ni electrode in a previous communication.[15] This article describes infrared spectroscopic measurements of the adsorbed species in both CO_2 and CO reduction on Ni and Fe electrodes in detail.

Experimental

Two kinds of phosphate buffer solutions were used as the electrolyte after preelectrolysis purification with a platinum black cathode overnight: One was 0.10 M KH_2PO_4 + 0.10 M K_2HPO_4 (1 M = 1 mol dm^{-3}) saturated with CO and Ar or N_2 (pH 6.8); the other was initially 0.05 M KH_2PO_4 + 0.15 M K_2HPO_4, which gave pH 6.8 after equilibration with saturated CO_2. The electrochemical equipment was a potentio-galvanostat (Tohogiken CO., Ltd., 2001) and a function generator (Tohogiken CO., Ltd., FG-02T). The electrode potential was measured with respect to a Ag/AgCl reference electrode; the potential values are given against SHE in this article. The counter electrode was a platinum wire.

A Nickel sheet (99.99% purity, thickness 0.2 mm) and an iron sheet (99.99% purity, thickness 0.1 mm) were cut to 10×12 mm, and attached with a lead strip of the same metal. The electrodes were polished to a mirror finish with alumina compounds down to 0.05 μm, and then degreased with acetone and electropolished in 85% phosphoric acid.

An infrared-electrochemical cell, originally designed by Bewick and his co-workers,[16] was partly modified in order to introduce an electrode from the upper part of the cell. The front side of the cell was attached with a CaF_2 optical window, and the back side with a glass syringe, which pushed the electrode against the window.

We measured two spectra at two different potentials at a time and represented the infrared spectra as the difference in them (subtractively normalized interfacial Fourier-transform infrared reflectance spectroscopy, SNIFTIRS).[17] The FT infrared measurements were conducted at ambient temperature by a JIR-6000 (Nihon Densi, Co., Ltd.) externally equipped with a MCT (mercury–cadmium–telluride) detector. The other details were described previously.[14)]

Results and Discussion

IR Spectra of Adsorbed Species on a Ni Electrode. The infrared spectra of adsorbed CO on the Ni electrode were acquired by the SNIFTIRS technique at -0.3 and -0.5 V vs. SHE. The results are presented in Fig. 1; the IR adsorption peaks at -0.3 V appear upward and those at -0.5 V downward.

Figure 1(a) gives the spectrum of the adsorbed CO obtained in a solution saturated with CO. Two bipolar peaks appear at ca. 2000 and 1900 cm^{-1}, suggesting that CO was adsorbed in two fashions, i.e. linear and bridged types. Eischens and co-workers initially proposed, that the C–O stretching frequency above ca. 2000 cm^{-1} can be assigned to linearly adsorbed CO, and that below 2000 cm^{-1} to bridged adsorption.[18)] The assignments were accepted in a recent review.[19)] Bipolar peaks indicate that the IR adsorption bands shift to lower wavenumber as the potential becomes more negative.

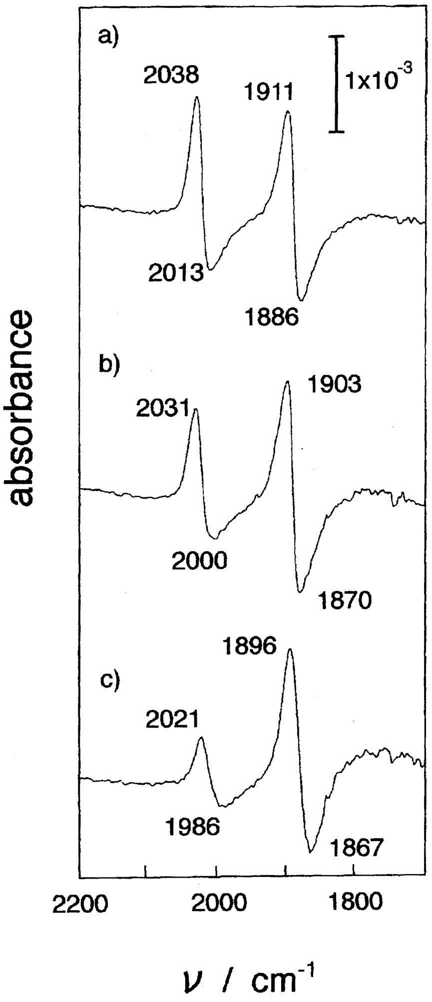

Fig. 1. SNIFTIRS spectra of a Ni electrode (-0.3 V vs. -0.5 V). a) Adsorbed CO in CO atmosphere. b) Adsorbed CO after removing the dissolved CO by N_2 sparging. c) Adsorbed CO after reduction of CO_2 at -1.2 V.

We previously showed that the cathodic current due to hydrogen evolution is greatly suppressed by adsorbed CO on a Ni electrode.[6)] The extent of the suppression of hydrogen evolution remained unchanged after the dissolved CO was purged by Ar sparging. This fact suggests that CO is strongly adsorbed on the Ni electrode surface, and is not easily desorbed. Figure 1(b) gives the spectrum of the Ni electrode surface on which CO was adsorbed from the electrolyte; then dissolved CO was purged by Ar sparging. The spectra (a) and (b) in Fig. 1 show little difference in the bipolar peaks of the adsorbed CO. Thus, the spectral measurements evidently confirm that CO was strongly adsorbed on the Ni electrode and not removed by Ar sparging.

The intermediate species in CO_2 reduction was investigated by the following procedure. The Ni electrode, initially separated form the CaF_2 window, was polarized at -1.2 V in a CO_2 saturated solution. Hydrogen evolution was rapidly suppressed by this treatment. The electrode was subsequently pushed against the window. Then, an IR spectroscopic measurement was carried out. The results is given in Fig. 1(c). The absorptions near to 2000 and 1900 cm^{-1} in Fig. 1(c) are similar to those in Figs. 1(a) and 1(b) of adsorbed CO. Thus, the adsorbed CO was evidently formed on the Ni electrode during CO_2 reduction.

The peak wavenumbers of the adsorbed species in Fig. 1(c) are shifted slightly lower, and the peak-to-peak heights are smaller compared with those in Figs. 1(a) and 1(b). These features indicate that the amount of adsorbed CO in CO_2 reduction may be less than those in CO reduction. According to Eischens and Pliskin,[18)] the adsorption bands of adsorbed CO on Ni in both linear and bridged fashion decrease as the coverage decreases. The adsorbed CO may be reduced to some extent at the potential where the reduction of CO_2 to CO proceeds, as discussed in the next section.

The potential-induced variations in the IR absorption of adsorbed CO were measured in a CO atmosphere. We attempted to minimize the overlapping of the spectra in the subtraction procedure in the SNIFTIRS technique by choosing a wide potential difference. The reference potential was -0.9 V for sample potentials more positive than -0.5 V, and the reference potential was -0.1 V for sample potentials more negative than -0.5 V. The anodic and cathodic currents were low in this potential range in a CO atmosphere.

The results are shown in Fig. 2. The peak wavenumbers are linearly related to the electrode potentials for both adsorbed species. The peak shift of the linearly adsorbed CO is approximately 57 cm^{-1}/V, and that of the bridged fashion is 61 cm^{-1}/V. The data for bridged CO slightly deviate downwards from the linear correlation near to 0 V. The deviation from the straight line in Fig. 2 may also come from the decrease of the adsorbed CO, because of partial oxidation of CO at the potential.[6)]

Reduction of Adsorbed CO at a Ni Electrode by Negative Polarization. The electrochemical and infrared spectroscopic measurements have confirmed that the adsorbed

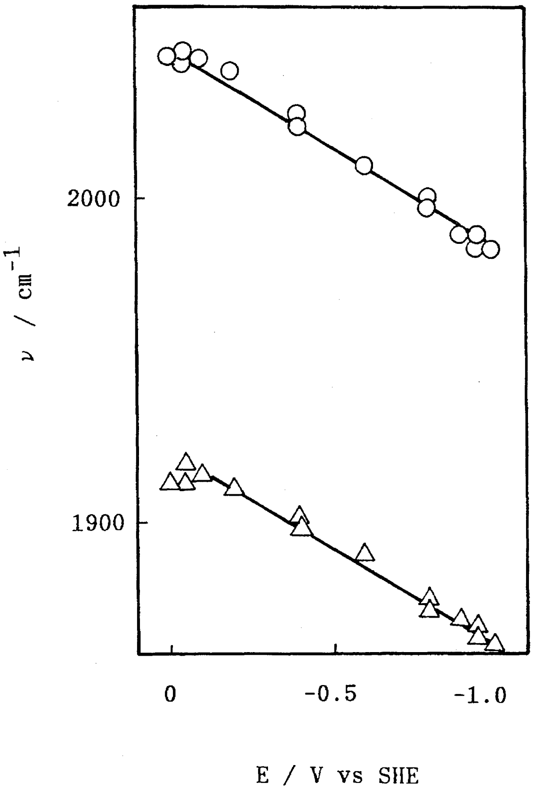

Fig. 2. Potential dependence of the C–O stretching vibrational frequency of CO adsorbed on a Ni electrode. (○): linear type, (△): bridged type.

CO is formed during CO_2 reduction. However, it still remains ambiguous whether the adsorbed CO is a real intermediate species, which is eventually reduced to hydrocarbons. Thus, negative polarization of the adsorbed CO was studied by infrared spectroscopy at ambient temperature.

CO was adsorbed at −0.4 V with the Ni electrode being kept apart form the IR window in a CO atmosphere, and the dissolved CO was purged with N_2. Then, the Ni electrode was polarized at −1.10 V for various prescribed times in a N_2 atmosphere, where hydrogen evolution proceeds. After polarization, the electrode was maintained at −0.4 V and pushed against the window. The SNIFTIRS operation was conducted at −0.3 and −0.5 V.

The results are shown in Fig. 3. The height of two bipolar peaks gradually decreases with polarization time. The adsorption peak for linearly adsorbed CO disappears after 9 min. The wavenumber also diminishes, probably because the coverage of the adsorbed CO was reduced. The decreased CO may have been converted to hydrocarbons at −1.10 V on the electrode. Free CO could not have been desorbed at a negative potential, since the products from CO_2 reduction did not contain any trace of CO.⁶⁾

Rate Constants of Desorption of CO from the Ni Electrode. The decay rate of linearly adsorbed CO is higher than that of bridged CO, as shown in Fig. 3. Infrared spectra could not be acquired at −1.10 V, since the hydrogen evolution proceeds considerably at this potential. Thus, we have to assume that the amounts of the adsorbates do not vary

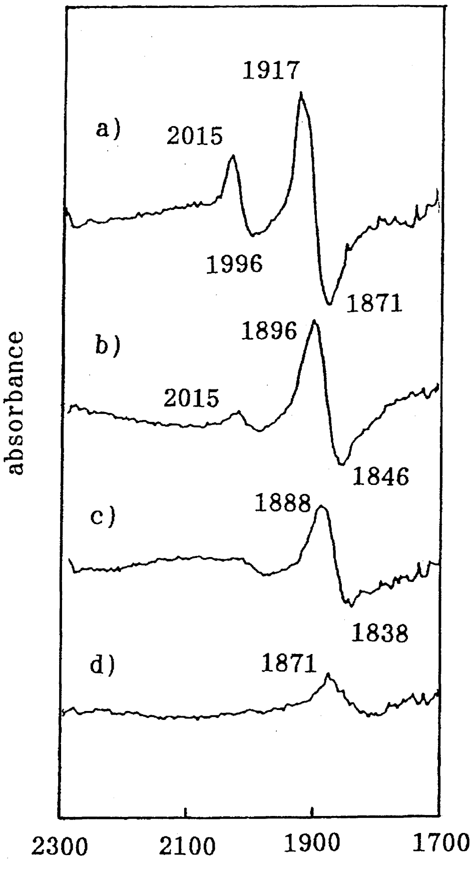

Fig. 3. SNIFTIRS spectra of adsorbed CO on a Ni electrode affected by the cathodic polarization at −1.10 V. Polarization time a) 0 min, b) 1 min, c) 2 min, d) 9 min.

between −0.3 and −1.10 V, although Chang and Weaver reported that the integrated absorbance of the bridged and linear C–O bands at Pt single-crystal electrodes varies with the potential and coverage.²⁰⁾

If the reduction proceeds in the first-order reaction with respect to the adsorbed species **a**, the logarithm of the amounts of **a** could decay linearly with the time, i.e.,

$$-\mathrm{d}\Gamma_a/\mathrm{d}t = k_a\Gamma_a, \qquad (1)$$

$$\therefore \ln \Gamma_a = b - k_a t, \qquad (2)$$

where k_a and Γ_a are the rate constant and the amounts of adsorbed species **a**, and b is a constant.

We assume that the peak to peak height (P–P) in the SNIFTIRS spectra is proportional to Γ_a. Figure 4 shows the natural logarithm of (P–P) plotted against the polarization times. The data are well correlated linearly, verifying the assumption of a first-order reaction. From the slopes of the two lines, the rate constants were obtained to be 1.7×10^{-2} s^{-1} for linearly adsorbed CO (k_L) and 5.1×10^{-3} s^{-1} for bridged CO (k_B). Identical experiments were repeated several times. Although linear correlations held in all cases, the value of the constants varied: k_L, 1.7—0.8×10^{-2} s^{-1}, k_B, 5.1—1.2×10^{-3} s^{-1}. The variations of the constants were

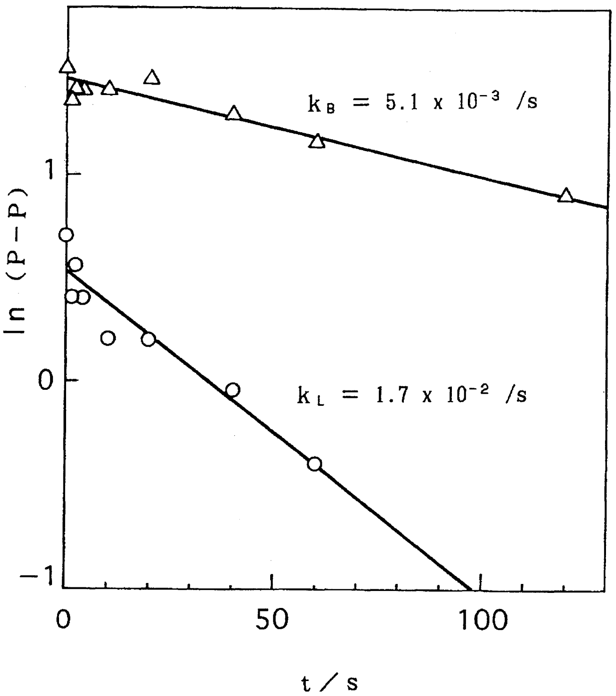

Fig. 4. The variations of the peak height of the infrared absorptions of both linear and bridged CO on a Ni electrode with the polarization time.

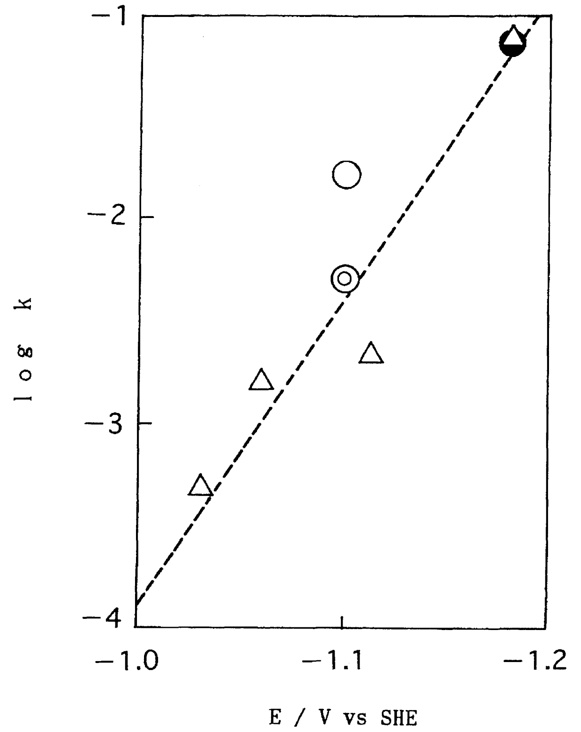

Fig. 5. The desorption rate constants of adsorbed CO from a Ni electrode.(○) linearly adsorbed CO, and (◎) bridgedly adsorbed CO as obtained in the present work. (●): Calculated from the reduction currents in CO electrolysis reported in the previous paper.[6] (△): Estimated from the time course of the prevention of hydrogen evolution under a cathodic polarization. The value at −1.18 V is cited from Ref. 21, and others are obtained in the present work.

probably due to some uncertainty in the separation between the electrode and the IR window. The value for linear CO is about three times higher than that for bridged CO. The bridged type may require a higher activation energy in the conversion of CO to hydrocarbons, since the bridged CO is coordinated with more surface atoms, compared with the linearly adsorbed CO.

The first-order rate constants for the decay of adsorbed CO were estimated by other procedures. The amounts of adsorbed CO may be obtained from the extent of prevention of hydrogen evolution. When a cathodic potential step is applied, hydrogen evolution is gradually promoted, since the adsorbed CO is removed from the electrode surface. Thus, the decay rate is derived from an analysis of the time course. The first-order rate constant was evaluated to be 7.91×10^{-2} s^{-1} at −1.18 V, as given in a previous paper.[21] According to an identical procedure, the rate constants were obtained for various potentials. The results are indicated by △ in Fig. 5, giving a well correlated straight line. The slope of the straight line is 67 mV/decade. This value suggests that the first electronation process is in electrochemical equilibrium and a subsequent elementary chemical process is the rate-determining step. The detailed reaction mechanism is under investigation.

A constant-current electrolysis of CO (2.5 mA cm^{-2}) at a Ni electrode led to various products, as reported in our previous publication;[6] the sum of the partial currents for these products amounted to 0.115 mA cm^{-2}, Since hydrogen evolution is totally prevented by CO adsorption, we can reasonably assume that the coverage of CO is unity. If we take the number of adsorption sites as 3.09×10^{-9} mol cm^{-2} (roughness factor 1, the number of surface nickel atoms for (111) plane[22]), we can estimate the first-order rate constant to be 6.8×10^{-2} s^{-1} from the total reduction rate of CO (2.1×10^{-10} mol cm^{-2} s^{-1}, as obtained from the partial current of CH_4, C_2H_4, C_2H_6, and C_2H_5OH[6]). The value is indicated by ● at −1.18 V in Fig. 5.

The present spectroscopic measurements give the rate constants of both linear and bridged types at −1.10 V, as plotted in Fig. 5 (○, ◎); they fall near to the correlation line. Good compatibility among the rate constants, determined by three different procedures, indicates that the adsorbed CO in both linear and bridged fashions are real intermediate species in the electrochemical reduction of CO to hydrocarbons.

We have reported that the reaction products from CO_2 reduction as well as the product distribution are similar to those from CO. The potentials of CO_2 electrolysis are sufficiently negative to reduce CO.[6] Adsorbed CO is formed from CO_2, as shown in Fig. 1, which is further reduced to hydrocarbons. Thus, we can reasonably conclude that the adsorbed CO is an intermediate species in CO_2 reduction as well.

Infrared Spectra of Adsorbed Species on an Fe Electrode. Spectroscopic measurements were made for adsorbed species on an Fe electrode surface as well. The SNIFTIRS operation was conducted at −0.5 and −0.7 V under a CO atmosphere. The potential of the electrode was kept at −0.7 V before IR measurements. Figure 6 shows the result that a single bipolar peak appears slightly below 2000 cm^{-1}. When the potential was not kept cathodically at the time of dipping, an upward shoulder peak (corresponding to the electrode potential of −0.5 V) at around 2020 cm^{-1} was occasionally observed. The shoulder peak did not appear when the electrode was kept at the cathodic potential.

Eischens et al. reported the peak to be at 1960 cm^{-1} in a Fe–CO gas system by infrared spectroscopy, and assigned it to linearly adsorbed CO.[23] Since then, many workers have studied Fe–CO systems, and have observed various peaks in the vicinity of 2000 cm^{-1}. Sheppard and Nguyen[19] reviewed these data. They assigned the band at ca. 2020 cm^{-1} to linearly adsorbed CO, that at ca. 1970 cm^{-1} to bridged CO, and other bands at higher wavenumbers, for example 2070 cm^{-1} or 2180 cm^{-1} etc., to adsorbed species on an oxidized Fe surface.[24,25] Eischens and Pliskin mentioned a difficulty in the complete reduction of iron samples.[23] It is difficult to relate these results to our aqueous results. Though the band is in a slightly lower region, we tentatively assigned the shoulder peak at 2020 cm^{-1}, observed with the electrode not polarized cathodically at the time of dipping, to species on the oxidized surface. The peak at around 1970 cm^{-1} is then assigned to CO on a Fe surface in the linear or bridged type.

Fe electrode produces similar hydrocarbons to those from Ni in CO reduction.[7] The spectrum observed in the reductive condition shown in Fig. 6 would be derived from an intermediate in hydrocarbon formation.

The wavenumber of the absorption peak varies with the electrode potential. Figure 7 presents the results on an Fe electrode obtained by a procedure identical to the measurements of the Ni electrode as above (Fig. 2). The reference potentials are −0.6 or −0.8 V, depending on the sample potential. The peak wavenumber decreases linearly as the potential becomes negative. The frequency shift is 55 cm^{-1}/V, close to that for the Ni–CO system. The deviations from a straight line above −0.3 V may be due to the partial oxidation of adsorbed CO, as previously mentioned concerning the Ni electrode.

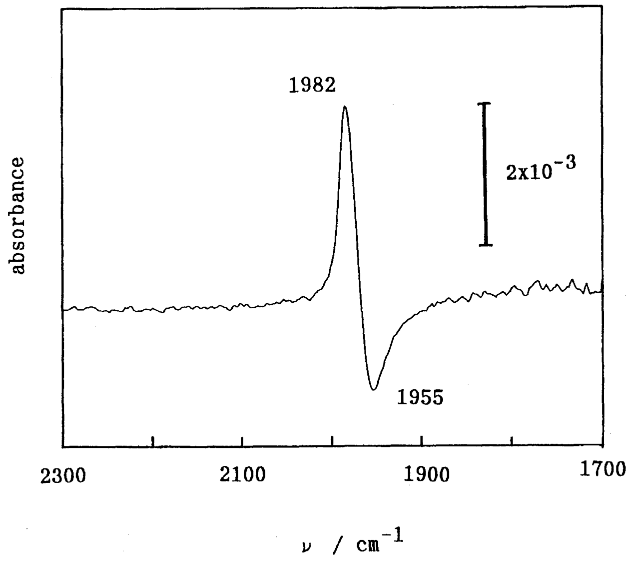

Fig. 6. SNIFTIRS spectra of adsorbed CO on an Fe electrode (−0.5 V vs. −0.7 V) in CO atmosphere.

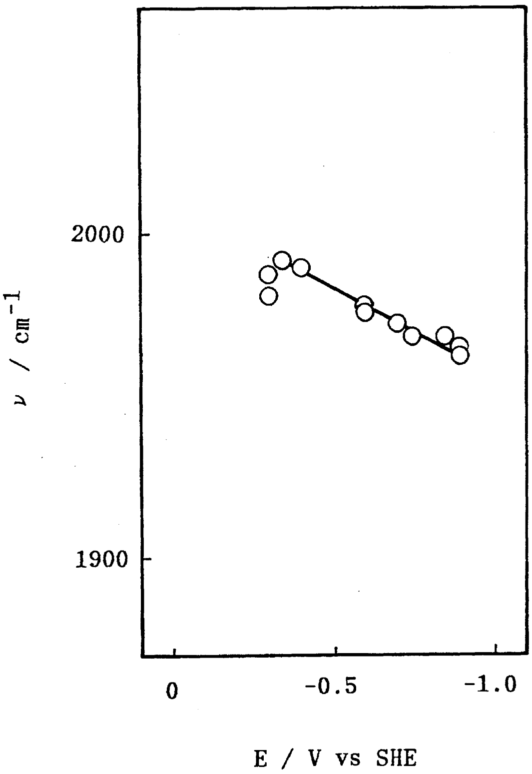

Fig. 7. Potential dependence of the C–O stretching vibrational frequency of CO adsorbed on an Fe electrode.

Nature of the Adsorbed CO as an Intermediate Species in CO Reduction. The potential dependence of the IR absorption peak of the adsorbed CO is affected by the coverage of CO.[20] In saturated adsorption, the values range between 30 cm^{-1}/V for a linearly adsorbed species[26] and 60 cm^{-1}/V for a bridgedly adsorbed species on Pt.[20] The present results for Ni and Fe are relatively higher in this range: 57 cm^{-1}/V for linear CO on Ni, 61 cm^{-1}/V for bridged CO on Ni, and 55 cm^{-1}/V for adsorbed CO on Fe. Some workers have reported relatively high values: for linearly adsorbed CO, Kunimatsu et al. observed 48 cm^{-1}/V on Pd[27] and 64 cm^{-1}/V on Au.[28] Ikezawa et al. reported approximately 50 cm^{-1}/V for linearly adsorbed CO on Pt, Pd, Au, and Ag in a neutral solution.[29] The potential dependence of the IR adsorption is closely related to the interaction between the adsorbed CO and metals: the Stark effect[30] or the back donation of electrons to the empty electronic orbitals from the electrode metal.[31] Systematic research of adsorbed CO on various metals is required under various conditions.

We previously reported on the absorption bands of CO adsorbed on a Cu electrode.[14] We can compare the results on three metal: Fe, Ni, and Cu. The order of the wavenumbers of adsorbed CO at −0.9 V is Cu: 2080 cm^{-1}>Ni: 2010 cm^{-1} (linear)>Fe: 1960 cm^{-1}>Ni: 1880 cm^{-1} (bridged). Blyholder and Allen related the C–O stretching band frequency of adsorbed CO with the adsorption strength to the metal.[32] Weak adsorption leads to a high C–O stretching frequency, approaching the value of the free CO molecule, i.e. 2140 cm^{-1}. Thus, the reverse order of the CO adsorption strength on the electrodes in aqueous solutions may be given by Cu > Ni (linear) > Fe > Ni (bridged). Bridged CO is not always more stable than linear CO, for example on Pt.[33,34] However, one may still expect that a high coordination number could lead to high chemical stability.

The infrared bands of adsorbed CO may be related to the activity in electrochemical reduction. Ni and Fe electrodes reduce CO to methane, ethylene and ethane electrochemically with 5 to 8% of the current efficiencies at a constant current density of 2.5 mA cm^{-2} (the electrode potentials are around −1.2 V).[6,7] The Cu electrode effectively reduces CO to hydrocarbons with a current efficiency of 50% at 2.5 mA cm^{-2} (the potential is −1.40 V).[3,4] Thus, the activity order in CO reduction is Cu > Ni≈Fe. Linear CO is more easily reduced than bridged CO on a Ni electrode. The order of the electrochemical activity of metals in CO reduction roughly agrees with the reverse of the adsorption strength of CO.

We demonstrated that the adsorption strength between CO and the electrode metals is closely related to the product selectivity in CO and CO_2 electroreduction, and that a moderate strength on a Cu electrode is suitable for the production of hydrocarbons.[35] Kim et al. compared the activity of CH_4 formation from CO_2 on a Cu electrode with that on a Ru electrode, and suggested that the low activity of Ru is due mainly to the high thermodynamic stability of the adsorbed CO.[36] The present results of IR spectroscopy evidently confirm the validity of our hypothesis.

This work was supported by the Tokyo Ohka Foundation for the Promotion of Science and Technology, and by the Grant-in-Aid for Scientific Research (C) No. 06640739 and the Grant-in-Aid for Scientific Research on Priority Areas Catalytic Chemistry of Unique Reactor Fields Nos. 07242212 and 08232217 form the Ministry of Education, Science, Sports and Culture.

References

1) Y. Hori, K. Kikuchi, and S. Suzuki, *Chem. Lett.*, **1985**, 1695.

2) Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, *Chem. Lett.*, **1986**, 897.

3) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, *J. Am. Chem. Soc.*, **109**, 5022 (1987).

4) Y. Hori, A. Murata, and R. Takahashi, *J. Chem. Soc., Faraday Trans. 1*, **85**, 2309 (1989).

5) Y. Hori, H. Wakebe, T. Tsukamoto, and O. Koga, *Electrochim. Acta*, **39**, 1833 (1994).

6) Y. Hori and A. Murata, *Electrochim. Acta*, **35**, 1777 (1990).

7) A. Murata and Y. Hori, *Denki Kagaku*, **59**, 499 (1991).

8) T. E. Teeter and P. V. Rysselberghe, *J. Chem. Phys.*, **22**, 759 (1954).

9) H. Noda, S. Ikeda, Y. Oda, K. Imai, and K. Ito, *Bull. Chem. Soc. Jpn.*, **63**, 2459 (1990).

10) A. W. B. Aylmer-Kelly, A. Bewick, R. Cantrill, and A. M. Tuxford, *Faraday Discuss., Chem. Soc.*, **56**, 96 (1973).

11) B. Beden, A. Bewick, M. Razaq, and J. Weber, *J. Electroanal. Chem.*, **139**, 203 (1982).

12) T. Iwasita, F. C. Nart, B. Lopez, and W. Vielstich, *Electrochim. Acta*, **37**, 2361 (1992).

13) Y. Hori, A. Murata, and Y. Yoshinami, *J. Chem. Soc., Faraday Trans.*, **87**, 125 (1991).

14) Y. Hori, O. Koga, Y. Yamazaki, and T. Matsuo, *Electrochim. Acta*, **40**, 2617 (1995).

15) Y. Hori, O. Koga, A. Aramata, and M. Enyo, *Bull. Chem. Soc. Jpn.*, **65**, 3008 (1992).

16) A. Bewick, K. Kunimatsu, B. S. Pons, and J. W. Russell, *J. Electroanal. Chem.*, **160**, 47 (1984).

17) A. Bewick and S. Pons, in "Advances in Infrared and Raman spectroscopy," ed by R. J. H. Clark and R. E. Hester, Wiley-Heyden, London (1985), Vol. 12.

18) R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956).

19) N. Sheppard and T. T. Nguyen, "Advances in Infrared and Raman Spectroscopy," Heydon, London (1978), Vol. 5, p. 67.

20) S-C. Chang and M. J. Weaver, *Surf. Sci.*, **238**, 142 (1990).

21) O. Koga and Y. Hori, *Electrochim. Acta*, **38**, 1391 (1993).

22) "American Institute of Physics Handbook," 3rd ed, McGraw-Hill, New York (1982).

23) R. P. Eischens and W. A. Pliskin, *Adv. Catal.*, **10**, 1 (1958).

24) M. J. Heal, E. C. Leisegang, and R. G. Torrington, *J. Catal.*, **51**, 314 (1978).

25) I. G. Voroshilov, N. K. Lunev, L. M. Roev, and M. T. Rusov, *Dopov. Akod. Nauk Ukr. RSR, Ser. B*, **1975**, 319; *Chem. Abstr.*, **83**, 103698b (1975).

26) K. Kunimatsu, H. Seki, W. G. Golden, and J. G. Golden, *Surf. Sci.*, **158**, 596 (1985).

27) K. Kunimatsu, *J. Phys. Chem.*, **88**, 2195 (1984).

28) K. Kunimatsu, A. Aramata, H. Nakajima, and H. Kita, *J. Electroanal. Chem.*, **207**, 293 (1986).

29) Y. Ikezawa, H. Saito, Matsubayashi, and G. Toda, *J. Electroanal. Chem.*, **252**, 395 (1988).

30) D. K. Lambert, *Solid State Commun.*, **51**, 297 (1984).

31) N. K. Ray and A. B. Anderson, *J. Phys. Chem.*, **86**, 4851 (1982).

32) G. Blyholder and A. C. Allen, *J. Am. Chem. Soc.*, **91**, 3158 (1969).

33) K. W. Frese, Jr., *Surf. Sci.*, **202**, 277 (1988).

34) R. P. Norton, J. W. Goodale, and E. B. Selkirk, *Surf. Sci.*, **83**, 189 (1979).

35) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, *Chem. Lett.*, **1987**, 1665.

36) J. J. Kim, D. P. Summers, and K. W. Frese, Jr., *J. Electroanal. Chem.*, **245**, 223 (1988).