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Infrared Spectroscopic Observation of Adsorbed CO Intermediately Formed in the Electrochemical Reduction of CO_2 at a Nickel Electrode

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A nickel electrode surface during electroreduction of CO_2 in phosphate buffer solution was studied by in situ infrared spectroscopy. SNIFTIRS (subtractively normalized interfacial Fourier transform infrared spectroscopy) technique showed the presence of adsorbed CO on the electrode surface between −0.4 and −0.8 V vs. NHE in CO saturated solution. The adsorbed CO was bonded to the electrode in linear and bridged fashions. Linear and bridged adsorbed CO molecules were also detected on the electrode during the electroreduction of CO_2. Linear CO disappeared at relatively negative potential (−0.8 V). Since the reduction of adsorbed CO proceeds below −1.0 V, the electroactive species in the reduction of CO is presumed to be bridged type CO.

Electrochemical reduction of CO_2 and CO effectively yields CH_4, C_2H_4, and alcohols in aqueous electrolytes with metallic copper electrodes as firstly demonstrated by the present authors.[1-4] Nickel is also an active electrocatalyst in the reduction of CO_2 and CO to CH_4, C_2H_4, and C_2H_6, although less active than copper;[5] the partial current of CO_2 and CO reduction at Ni is approximately 0.1 mA cm^{-2}. These hydrocarbons may be formed with intermediate formation of CO reduced from CO_2 as indicated in the case of copper electrodes on the basis of the voltammetric and coulometric measurements in aqueous electrolytes.[6]

CO is strongly adsorbed on Ni from CO saturated electrolytes,[7] and adsorbed CO is readily oxidized at 0.12 V vs. NHE in the anode stripping measurements.[5] Adsorbed CO is also formed in the electroreduction of CO_2 at Ni and anodically oxidized at 0.12 V. The adsorbed CO on Ni markedly prevents the cathodic hydrogen formation, eventually reduced to hydrocarbons such as CH_4 and C_2H_6.[5] These experimental facts indicate that the intermediate formation of adsorbed CO from CO_2 on Cu and Ni electrode surface has been well established by the electrochemical measurements. It is interesting whether or not the adsorbed species are detected by spectroscopic measurements, which may reveal the molecular and electronic nature of the adsorbed species.

The papers which report in situ reflective IR spectroscopic measurements of electrode surface have concentrated on platinum group metal electrodes, since strong IR signals are advantageously obtained from these electrode surfaces. Few articles have been published which report in situ IR spectroscopic measurements with Ni electrodes. A small number of publications have reported IR spectroscopic data with regard to the electrochemical reduction of CO_2 on metallic electrodes.

Beden et al. reported a spectroscopic study of electrochemically reduced CO_2 species at a Pt electrode in 1 M H_2SO_4 (1 M=1 mol dm^{-3}).[8] They revealed that CO is formed from CO_2 and strongly bonded on the Pt surface. They presumed that $COOH_{ad}$ or COO^- is intermediately produced in the reduction of CO_2 to CO.

Bockris and his co-workers reported in situ IR spectroscopic study of electrochemical reduction of CO_2 at *p*-CdTe[9] and Pt.[10] They claimed that they obtained spectra assigned to adsorbed $CO_2^{\cdot-}$. McQuillan et al. studied an in situ laser Raman scattering measurement of electroreduction of CO_2 at an Ag electrode.[11] They observed spectra which were assigned to adsorbed carboxy species.

Aylmer-Kelly et al.[12] conducted an in situ IR-vis spectroscopic measurement of a Pb electrode surface during CO_2 reduction in aqueous and nonaqueous electrolytes. They found that spectral absorptions assigned to $CO_2^{\cdot-}$ were observed in the reaction and the spectrum was not altered from that obtained for free $CO_2^{\cdot-}$. Thus they concluded that $CO_2^{\cdot-}$ in the reaction is not adsorbed on the electrode.

This paper firstly reports an IR spectroscopic evidence of adsorbed CO formed on an Ni electrode surface during the electrochemical reduction of CO_2.

Experimental

Two kinds of phosphate buffer solutions (pH 6.8) were used as the electrolyte after preelectrolysis purification with a Pt black cathode overnight; the one is 0.10 M KH_2PO_4+0.10 M K_2HPO_4, pH 6.8 saturated with CO, and the other is initially 0.05 M KH_2PO_4+0.15 M K_2HPO_4, pH 6.8 after equilibration with saturated CO_2.[4-6] A nickel disk (99.99% purity, the diameter 12 mm, thickness 0.2 mm) was used as the electrode for the IR measurement after degreasing and electropolishing. The electrode potential was measured with respect to an Ag/AgCl reference electrode, and the potential value is given against NHE in the followings. The counter electrode is a Pt wire. The electrolytic cell is equipped with an Si window. The previous publications gave descriptions of the other details of the spectroscopic measurements.[13,14] The FT infrared spectrometric data acquisitions were carried out (500 scans, 4 cm^{-1} resolution) at ambient temperature by Perkin Elmer model 1720X FT-IR, which is externally equipped with an MCT (mercury cadmium telluride) detector cooled to liquid N_2

temperature.

Results and Discussion

CO_2 is not reduced at potentials more positive than −0.4 V at Ni electrode.[5)] Thus an infrared reflective spectrum was initially measured as a reference at −0.4 V under CO_2 atmosphere, where the Ni electrode is free from adsorbed CO. The potential was subsequently scanned between −0.4 and −1.2 V at 50 mV s^{-1} two to three times, and then brought to the potential at which the measurement was made. The previous studies[5)] showed that the cathodic scanning down to −1.2 V gives rise to adsorbed CO or related species as confirmed by the significant prevention of cathodic hydrogen formation.

Figure 1 presents the spectra obtained at −0.4 V (a) and −0.8 V (b). Absorptions appear at 1895 cm^{-1} in (a) and 1855 cm^{-1} in (b), respectively. The absorptions are weak among noises due to the strong infrared absorptions of ambient water vapor and the electrolyte. Since CO adsorbed on Ni gives relatively broad IR spectra in accordance with Eischens et al.,[15)] sharp spectroscopic absorptions will hardly be obtained in electrochemical systems as well.

However, the absorption at 1895 cm^{-1} of the spectrum (a) at −0.4 V obtained before and after the measurement of (b) at −0.8 V agreed well with each other. Thus the presence of the absorptions at 1895 cm^{-1} at −0.4 V and 1855 cm^{-1} at −0.8 V may be taken as unequivocal.

We applied SNIFTIRS (subtractively normalized interfacial Fourier transform infrared spectroscopy) technique to the present system. The spectroscopic measurements were performed at two different potentials without changing the atmosphere. Figure 2 presents the difference between the two spectra at −0.4 V and −0.8 V obtained under CO and CO_2 respectively. The absorptions at a relatively positive potential (−0.4 V) appear as upward peaks, and the ones at a relatively negative potential (−0.8 V) as downward ones. Spectra measured under CO and CO_2 in Fig. 2 show similar features near 2000 and 1900 cm^{-1}. Thus the species adsorbed on the Ni electrode during the CO_2 reduction must be closely related to the one adsorbed from CO atmosphere.

The bipolar peak from 1850 to 1900 cm^{-1}, corresponding to the absorptions shown in Fig. 1, is assigned to CO adsorbed in bridged fashion by reference to the IR spectrum data obtained in gas phase adsorption measurements.[16,17)] The appearance of the bipolar peak indicates that the IR absorption shifts to lower wavenumber with increase of the negative potential. The shift rate is 60—90 cm^{-1} V^{-1} as estimated from Fig. 2, much higher than that observed for linear CO at Pt (30 cm^{-1} V^{-1}).[18)] The dependence of the absorption frequency upon the potential is explained in terms of chemical bonding and electric field interactions.[18)] The reason of discrepancy between the present value and the reported one is unknown at present.

The peak at ca. 2000 cm^{-1} is assigned to linear adsorbed CO according to the reported spectroscopic data.[16,17)] Since the peak at ca. 2000 cm^{-1} is a monopolar one, the linear CO may disappear at −0.8 V by some transformation to bridged one. The interconversion of linear

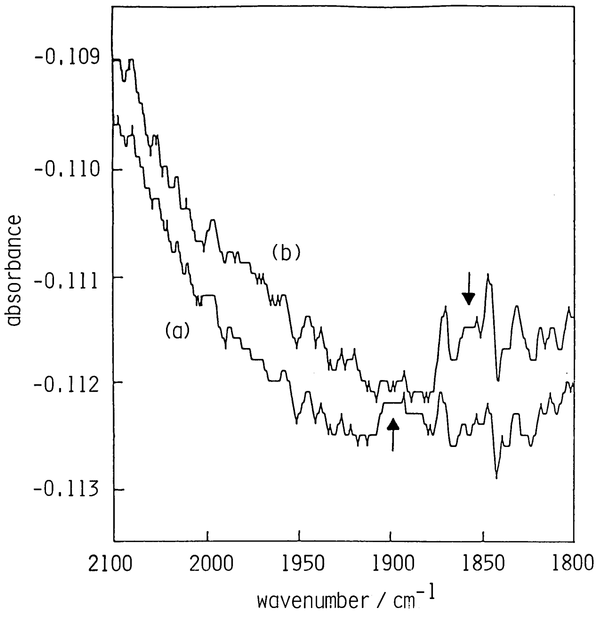

Fig. 1. In situ reflected infrared spectra of an Ni electrode surface in the electrolyte of phosphate buffer solution (pH 6.8) saturated with CO_2 at −0.4 V (a) and −0.8 V (b) after cathodic scanning to −1.2 V vs. NHE. The spectra are presented with reference to the spectrum at −0.4 V without the cathodic scanning. The peaks pointed by arrows are 1895 cm^{-1} (a) and 1855 cm^{-1} (b).

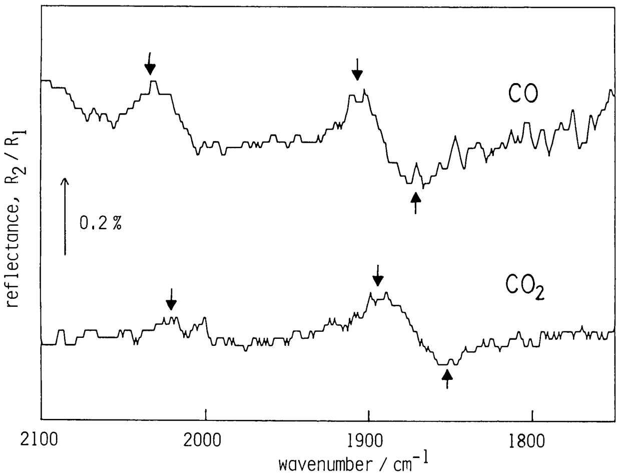

Fig. 2. SNIFTIRS spectra obtained from an Ni electrode surface in CO and CO_2 atmospheres. The spectra are given in the reflectance ratio R_2/R_1, where R_1 refers to the reflectance at −0.4 V and R_2 at −0.8 V. The spectrum of CO_2 was obtained after a cathodic scanning to −1.2 V vs. NHE. The peaks pointed by arrows are 1870, 1905, and 2030 cm^{-1} for CO saturated solution; 1855, 1895, and 2015 cm^{-1} for CO_2 saturated solution.

and bridged adsorbed CO has been already reported with a Pt electrode.19) The electroreduction of CO, scarcely observed at −0.8 V, proceeds below −1.0 V vs. NHE in phosphate buffer electrolyte.5) Thus the bridged CO may be the active species in the electroreduction of CO to hydrocarbons.

The IR absorptions both for linear and bridged CO adsorbed from CO_2 take place at lower wavenumbers by ca. 20 cm^{-1} than those from CO. The difference may be ascribed to either of the following two reasons. Firstly, the species adsorbed during CO_2 reduction may not be identical to the one obtained in CO atmosphere. However, both species must be closely related with each other, since the adsorbed species both from CO and CO_2 are electrochemically oxidized at the same potential.5)

Secondly, the adsorbed C–O vibrational stretching band depends markedly upon the coverage.20–22) The electrode potential is brought to −1.2 V for CO_2 system before the IR measurement in order to obtain adsorbed CO from CO_2 as mentioned above. Adsorbed CO may be reduced to some extent at −1.2 V, and the coverage of adsorbed CO will naturally be lower than that from CO saturated solution. The vibrational frequencies of C–O stretching increase with the coverage as reported previously.20–22) Thus the C–O stretching frequencies obtained from CO_2 reduction will shift to lower wavenumbers.

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