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FT-IR Spectrometry of the Reduced CO_2 at Pt Electrode and Anomalous Effect of Ca^{2+} Ions

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The IR spectrum of the reduced CO_2 was confirmed to be assigned as the adsorbed CO, and received an anomalous ca. 30 cm^{-1} downward shift by the addition of Ca^{2+} ions at very small concentration in a 0.1M sulfuric acid solution. The change of voltammogram characteristics due to Ca^{2+} ions was observed in the presence of CO_2, but not in its absence.

Carbon dioxide, which has a quite essential role in biological system and is expected to be activated and/or fixed from environmental point of view, is known to adsorb on Pt in a reduced form, as at the first time proposed by Giner.[1)] Although anions have been recognized to play an important role as specifically adsorbed species in an electric double layer at electrode-electrolyte interface,[2)] various biological processes are under the control of movement of cations,[3)] and Ca^{2+} ions were recently observed to give a significant influence to spectral features of the adsorbed CO from CO gas in sulfuric acid solution.[4)] Horànyi and Rizmayer also reported the adsorption of Ca^{2+} ions on Pt at hydrogen adsorption potential region in various acidic solutions by radiotracer method.[5)] Spectrum of the adsorbed CO_2 from CO_2 gas was recently reported to be observed at wavenumber of 2370 cm^{-1} by in situ FT-IR method with a ZnSe window.[6)] In order to confirm the nature of the reduced CO_2[7)] and the results of Ref. 6 by IR spectrometry, we have carried out IR spectroscopy and voltammetry together with the study of the effect of Ca^{2+} ions.

In the case of in-situ infrared absorption spectroscopy, the adsorbed CO species was first observed on Pt electrode through IR window of Si by electrode potential modulation method.[8)] Later, the CaF_2 prism window replaced an Si window,[9)] since the former IR characteristics are more suitable for in situ IR spectroscopy. However, as Ca^{2+} ions at very small concentration were found to affect the feature of the adsorbed CO from CO gas,4) we used an Si window in the present work. The cell employed was described elsewhere, together with experimental conditions.4,10) A single beam Perkin-Elmer 1720X FT-IR Spectrometer, optionally equipped with a InSb or MCT detector at liquid nitrogen temperature, was used. The IR spectrum at electrode potential of E = 0.7 V (vs. RHE to be abbreviated in the followings) in a nitrogen saturated 0.1 M H_2SO_4 was chosen as a background spectrum. Then, the spectrum at each potential was successively taken after the Pt electrode was subjected to the adsorption of CO_2 for 10 min at E = 0.05 V in a CO_2 saturated 0.1 M H_2SO_4 solution.

In order to observe the effect of Ca^{2+} ions on the CO_2 adsorption, we employed 10^{-4} M CaF_2 + 0.1 M H_2SO_4 and 10^{-3} M $CaSO_4$ + 0.1 M H_2SO_4 solutions. The results of voltammograms in the latter solution are shown in Fig. 1. In the hydrogen adsorption region, the cyclic voltammogram (CV) in the presence of CO_2 under anodic potential-sweep condition without Ca^{2+} ions was observed to be nearly identical to voltammogram after 5 min or more polarization at 0.05 V of Fig. 1. In the presence of Ca^{2+} ions, the CV at 0.1 V/s had two sharp peaks due to hydrogen adsorption although their current densities decreased due to the presence of CO_2 in Fig. 1. After the electrode potential was kept at 0.05 V for a certain period, the peaks of the adsorbed hydrogen became small due to CO_2 adsorption. These indicate that the decrease of the adsorption rate was caused by the addition of Ca^{2+} ions into sulfuric solution. The spectrum observed at 2370 cm^{-1} in Ref. 6 was neither observed nor any adsorbed CO_2 species as spectrum which is electrode potential-dependent. Instead, we observed IR spectra in spectrum region of the adsorbed CO at 2074 - 2078 cm^{-1} in the absence of Ca^{2+} of Fig. 2A, which located in the lower wavenumber region than the spectra of the adsorbed CO from CO gas.4) In the D_2SO_4/D_2O system, we observed the spectra of the reduced CO_2 at 2051 - 2065 cm^{-1}, of which the different peak position from H_2SO_4/H_2O system is taken to be due to solvent isotope effect. These results clarified that the reduced CO_2 is in the form of the adsorbed CO, of which the adsorption is assigned to be a linear CO on the Pt surface. The additional spectra at $2000\text{-}1300^{-1}$ were not observed within the present experimental condition.7)

By the addition of 10^{-4} or 10^{-3} M Ca^{2+} ions into sulfuric acid solution, the spectrum peak was shifted to lower wavenumbers by 23 or 28 cm^{-1} at 0.05 V, respectively, and its width was changed from <u>ca</u>. 14 to 19 cm^{-1} with Ca^{2+} ion addition, as shown in Fig. 2A - C. The shift of the peak was plotted with respect to electrode potentials in Fig. 3. We found there that the shift of the peak by an increase of electrode potentials took place to higher wavenumber region and then reversely to lower wavenumber region with

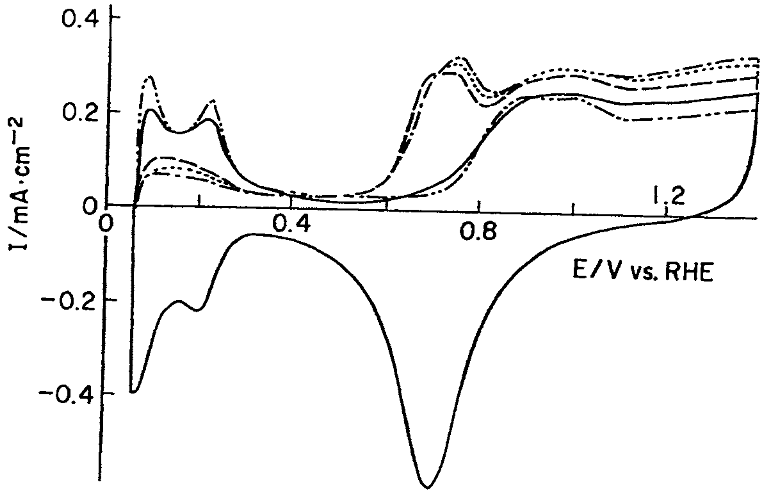

Fig. 1. Voltammograms at 0.1 V/s on Pt in 10^{-3} M $CaSO_4$ + 0.1 M H_2SO_4 at room temperature.
-·-·-·- and ——— for cyclic voltammograms under N_2 and CO_2 atmospheres, respectively. - - -, ·····, and -·-·- for voltammograms under CO_2 atmosphere after electrode potentials are kept at 1, 2, 5 min or more, respectively.

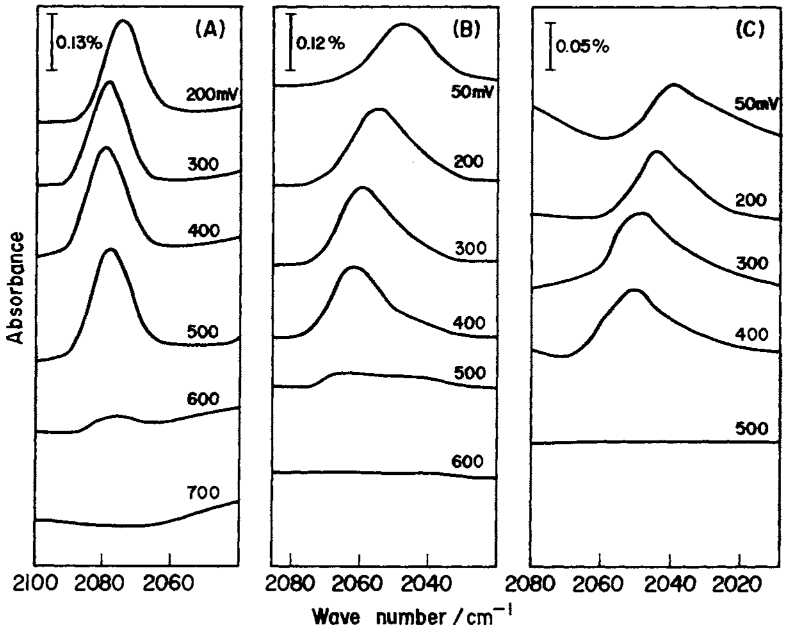

Fig. 2. In-situ IR spectra at various potentials of Pt electrode.
Indicated numbers in the figure are electrode potentials with respect to RHE. (A) 0.1 M H_2SO_4, (B) 10^{-4} CaF_2+ 0.1 M H_2SO_4, and (C) 10^{-3} M $CaSO_4$ + 0.1 M H_2SO_4.

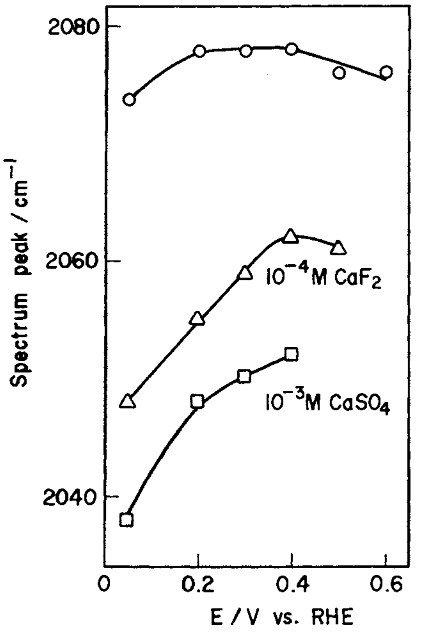

Fig. 3. Spectral peak position under CO_2 atmosphere against electrode potentials on Pt. ○ for 0.1 M H_2SO_4; △, 10^{-4} M CaF_2 + 0.1 M H_2SO_4; □, 10^{-3} M $CaSO_4$ + 0.1 M H_2SO_4.

an increase of electrode potential. The shift of the peak was 50 ± 2 cm^{-1}/V by electrode potentials at potential range ≤ 0.3 V, which is about twice as large as the case of the adsorbed CO from CO gas.4) From the observation of the decrease of spectrum peak intensity with respect to electrode potentials, the reduced CO_2 in the presence of Ca^{2+} ions was found to desorb 100 mV more negative than the case in their absence. These results indicate that Ca^{2+} ions are concentrated or adsorbed at the interface of the Pt electrode, as found by radiotracer method,5) and affect the adsorption state of the reduced CO_2.

Although voltammograms in the absence of CO_2 did not receive any influence of Ca^{2+} ions,4) the voltammograms and the spectra of the reduced CO_2 were changed with the presence of Ca^{2+} ions. The effect by Ca^{2+} in the vicinity of the electrode interface is tentatively discussed to weaken the C-O bonding of the reduced CO_2, being observed by a shift of the spectra to a lower wavenumber. The additional measurement with the other cations will assist in revealing the further features of the structure of the reduced CO_2 at the double layer interface.

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