



BNL-103787-2014-CP

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Presented at the 247th American Chemical Society National Meeting, Dallas TX

March 2014

**Chemistry Office
Brookhaven National Laboratory**

**U.S. Department of Energy
Office of Science**

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TRANSIENT SPECTROSCOPIC INVESTIGATIONS OF INTERMEDIATES INVOLVED IN CO₂ REDUCTION UNDER SUPERCRITICAL CO₂ CONDITIONS

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Introduction

Due to increasing concerns about global warming caused by the burning of fossil fuels, the conversion of abundant molecules such as CO₂ and H₂O into clean fuels and industrially important chemicals is a key scientific challenge of this century. The use of sunlight to drive these reactions in so-called artificial photosynthetic processes would provide a sustainable pathway to carbon-neutral fuels due to the abundance of available solar energy. Since CO₂ is the end product of combustion and therefore a very stable molecule, its conversion into higher energy forms requires the use of catalysts. One family of catalysts that has been shown to selectively reduce CO₂ to CO (an industrially important fuel precursor and intermediate) upon visible light irradiation in the presence of a sacrificial electron donor has the general formula, *fac*-[ReX(bpy)ⁿ(CO)₃]ⁿ⁺ (X = halide, phosphite, *etc.*; bpyⁿ = 2,2'-bipyridine and its derivatives; n = 0 or 1).¹ Quantum yields for CO production as high as 0.59 have been reported.² However, the catalytic reactions are very slow with typical turnover frequencies (TOFs) on the order of 1-12 h⁻¹. In addition, the formation of side products leads to rapid deactivation of the catalyst, with typical turnover numbers (TONs) of only ~10-25 for the mononuclear catalysts.

We have recently demonstrated a significant enhancement in catalytic activity through the use of a high concentration of CO₂ (15.5 M) in the form of supercritical CO₂ (scCO₂), mixed with *N,N*-dimethylformamide (DMF) in a single-phase, high-pressure reaction environment.³ We also found that the catalytic activity increases linearly with [DMF]. Using *fac*-ReCl(bpy)(CO)₃ as the catalyst, this resulted in an optimized TON of 62 at 17.8 MPa CO₂ / 60 °C / [DMF] = 6.3 M, and an initial TOF of 56 h⁻¹, which is a significant improvement over previous ambient pressure studies.

In order to more fully understand the enhanced catalytic activity under scCO₂ conditions, and the role of DMF in the reaction mechanism, we have started using a combination of nano- to millisecond UV-vis transient absorption and time-resolved infrared (TRIR) spectroscopy to probe the individual reaction steps in the catalytic cycle following light absorption. Such investigations are crucial since they will aid the design of new catalysts for use with scCO₂ with enhanced stability and activity. Preliminary results of these transient spectroscopic investigations are presented here.

Results and Discussion

Fig. 1 shows a series of TRIR spectra recorded with step-scan FTIR spectroscopy after 355 nm excitation of *fac*-ReCl(bpy)(CO)₃ in DMF in the presence of 1 M triethylamine (TEA). Immediately after excitation, two new ν(CO) bands (labeled as MLCT) are observed, corresponding to the metal-to-ligand charge transfer (MLCT) excited state of the complex. These rapidly decay into three new bands at 1995, 1881 and 1862 cm⁻¹ (labeled as OER), which correspond to the

one-electron reduced complex, *fac*-[ReCl(bpy)(CO)₃]⁻. This is the first step of the catalytic cycle for photocatalytic CO₂ reduction with this catalyst. The second step involves the ejection of the Cl⁻ ligand from the OER to generate a solvated species, *fac*-Re(bpy)(CO)₃(DMF).

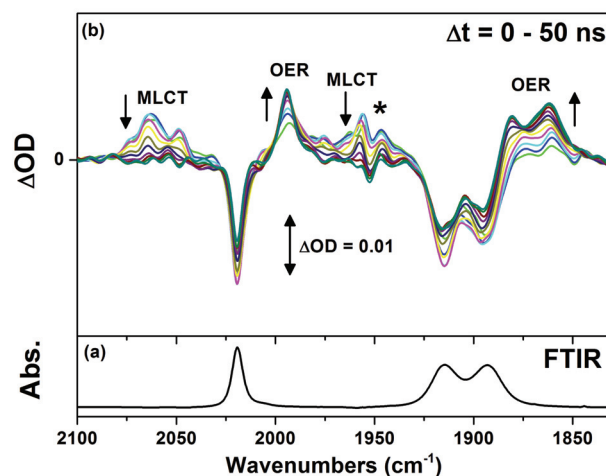


Fig. 1. (a) FTIR of *fac*-ReCl(bpy)(CO)₃ in DMF in the presence of 1 M TEA. (b) Time-resolved step-scan FTIR spectra obtained in the first 50 ns after 355 nm laser flash photolysis of this solution.

We have used TRIR spectroscopy to monitor the kinetics of the ejection of Cl⁻ from the OER in DMF under both ambient pressure conditions and scCO₂ conditions. Fig. 2 shows quantum-cascade laser TRIR kinetic traces recorded at 1863 cm⁻¹, corresponding to the OER. The decay of these traces represents the Cl⁻ ejection process from the OER. There is a striking difference between the kinetic trace recorded under ambient pressure (0.1 MPa N₂) and those recorded under scCO₂ conditions (p = 8.9 – 30.5 MPa, T = 40 °C). At ambient pressure, the observed rate of decay is 0.15 s⁻¹, whereas under high-pressure conditions the decay rate is much higher and is observed to increase slightly with pressure (9.85 s⁻¹ @ 8.9 MPa to 16.2 s⁻¹ @ 30.5 MPa).

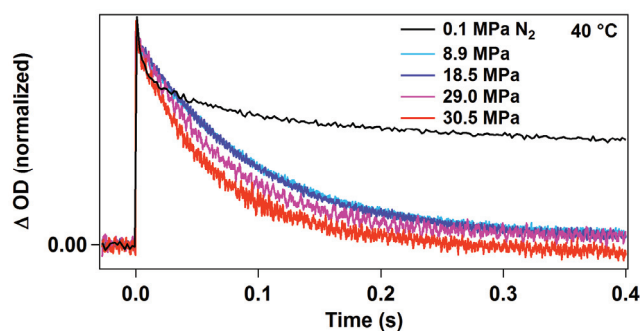


Fig. 2. Quantum-cascade laser TRIR kinetic traces recorded at 1863 cm⁻¹ after 355 nm excitation of *fac*-ReCl(bpy)(CO)₃ in DMF in the presence of 1 M TEA. The black trace was recorded under ambient pressure of N₂, which the colored traces were recorded in the presence of high-pressure scCO₂ at the indicated pressures.

Experimental

The apparatus for time-resolved step-scan FTIR spectroscopy has been described previously.⁴ Quantum-cascade laser TRIR kinetic traces were measured using a CW mode-hop-free external-cavity

quantum cascade laser (Daylight Solutions, 21052-MHF, 80 mW max. power) as a mid-IR source, and the third harmonic of a pulsed Nd:YAG laser (Continuum, Powerlite 7010, 355 nm, 5 ns.) as the excitation source. The IR probe beam was attenuated by a circular variable ND mid-IR filter (Reynard Corporation, R05600-40), focused through the sample cell and recollimated by a pair of off-axis parabolic mirrors (Thorlabs, MPD254762-90-P01), and then focused by another off-axis parabolic mirror (Thorlabs, MPD254254-90-P01) onto a fast risetime IR detector (Kolmar Technologies, KMPV10-1-J2 with 20 MHz AC/DC-coupled pre-amplifier). The DC-coupled signal from the detector was digitized by a 12-bit oscilloscope (Teledyne LeCroy, HRO 66Zi) and transferred to a PC for processing by custom LabVIEW software. The high-pressure spectroscopic cell for TRIR measurements was described in the Supporting Information of a previous publication.⁵

Conclusions

Since the loss of Cl⁻ from the OER is an extremely slow process, it is one of the limiting factors in the rate of catalytic CO₂ reduction with *fac*-ReCl(bpy)(CO)₃. Our preliminary results indicate that the loss of Cl⁻ is accelerated dramatically under high-pressure scCO₂ conditions, and this may be a contributing factor in the observed enhancement of catalytic activity under high-pressure scCO₂ conditions. However, subsequent reactions that follow the loss of Cl⁻ have also been shown to have extremely small rate constants,^{1c,6} and these are the rate limiting steps in CO₂ reduction. We are therefore currently working to extend our high-pressure TRIR investigations to examine these later reaction steps as a function of CO₂ pressure, in order to determine the reason for the enhanced catalytic activity observed under scCO₂ conditions.

Acknowledgement. H.K. is funded by the Japan-U.S. cooperation project for research and standardization of Clean Energy Technologies, The Ministry of Economy, Trade and Industry (METI), Japan. D.C.G. is funded under Contract DE-AC02-98-CH10886 with the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. We thank Dr. Etsuko Fujita (Brookhaven National Laboratory) for helpful discussions. We also thank Ms. Saeko Yaeshima for her support in our experiments.

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