

Photochemical CO₂ Splitting by Metal-to-Metal Charge-Transfer Excitation in Mesoporous ZrCu(I)-MCM-41 Silicate Sieve

Wenyong Lin and Heinz Frei*

Physical Biosciences Division, Mailstop Calvin Laboratory, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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The photoreduction of CO₂ by H₂O is one of the key chemical reactions for the generation of renewable fuels using light as an energy source. It was first reported in heterogeneous systems using excitation of large band gap semiconductor materials such as TiO₂, SrTiO₃, ZnO, or SiC with UV photons.^{1,2} Methanol and methane were detected upon prolonged irradiation along with varying amounts of CO, formic acid, and O₂ (recovery of the latter was met with mixed success).^{3,4} Use of smaller band gap particles such as ZnSe, CdS, CdSe, etc. allowed photoreduction of CO₂ with visible instead of UV light.⁵ However, organic donors or other sacrificial reagents were required.^{6–8} Because of the need for sacrificial reagents, a concept for visible light-induced CO₂ reduction by H₂O based on these results has thus far remained elusive.

Ligand-to-metal charge-transfer (LMCT) excitation of isolated Ti centers of framework-substituted micro- or mesoporous silicates by UV light was recently found by Anpo and co-workers to reduce CO₂ by H₂O at substantially better efficiency than dense-phase TiO₂ particles.⁹ Prolonged photolysis gave CH₃OH and CH₄ as the main products. We have shown by in situ FT-IR and mass spectrometric monitoring of the reaction (using Ti-substituted MCM-41 sieve) that CO and O₂ are the initial single-photon redox products.¹⁰ Use of isolated tetrahedral Ti centers on nanoporous support is a promising development for CO₂ photoreduction by H₂O, but no results have been reported so far that would allow us to utilize visible instead of UV photons for accomplishing the reaction at such metal centers. We have recently presented spectroscopic evidence that Ti centers can be activated by visible light when they are part of an oxo-bridged metal-to-metal charge-transfer (MMCT) moiety covalently anchored on the pore surface of MCM-41 silicate sieve (Ti–O–M, M = Cu(I) or Sn(II)).¹¹ In this approach, the center M acts as electron donor. Here, we report the first visible light-absorbing MMCT redox site that is capable of splitting CO₂ to CO. The site consists of Zr(IV) oxo-bridged to Cu(I), covalently anchored on the pore surface of MCM-41 sieve.

Assembly of covalently anchored ZrCu(I) moieties on the MCM-41 pore surface was accomplished by first grafting tetrahedral Zr centers using the established ZrCp₂Cl₂ precursor method.^{12–14} Subsequent removal of the remaining organic ligand by calcination is known to result in tripodally anchored ZrOH groups (Si/Zr = 24 per ICP-AES analysis).^{12,15} This was followed by addition of 0.2 g of Zr-MCM-41 crystallites so produced to a solution of Cu⁺(NCCH₃)₄PF₆ in 100 mL of CH₂Cl₂ (0.3 wt %) under a nitrogen atmosphere. The mixture was stirred at 40 °C for 30 min, filtered, and washed (Zr/Cu = 1.3). Monometallic Cu(I)-MCM-41 was prepared by the same procedure using the neat silicate as starting material (Si/Cu = 64). As-synthesized product was heated to 300 °C for 12 h under vacuum in order to remove residual CH₃CN ligands, which was verified by FT-IR spectroscopy.¹¹ The diffuse reflectance spectrum (DRS) of a pressed wafer of ZrCu(I)-MCM-41 shows an optical absorption extending into the visible region, as can be seen in Figure 1a. This new chromophore is more clearly

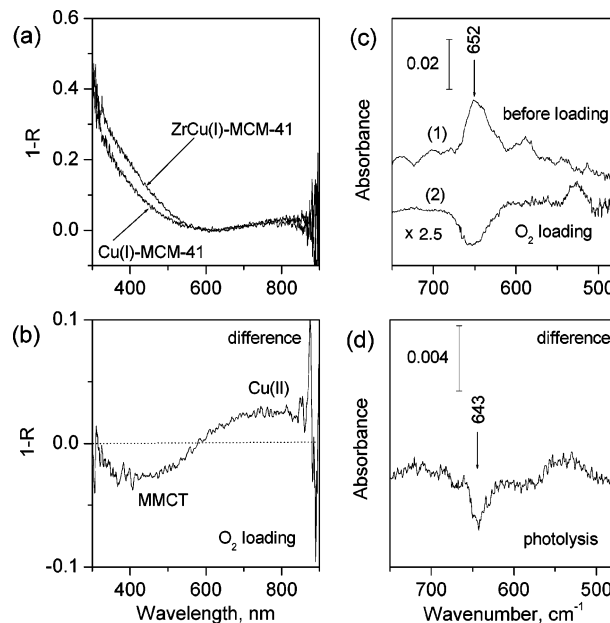
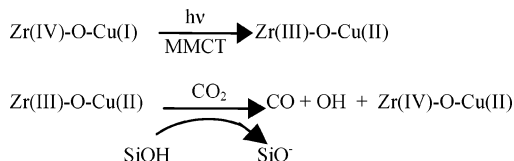


Figure 1. (a) UV-vis DRS of ZrCu(I)-MCM-41 and Cu(I)-MCM-41. (b) Difference DRS spectra recorded after and before exposure of ZrCu(I)-MCM-41 to O₂ gas (1 atm) at room temperature for 8 h. (c1) FT-IR spectrum of ZrCu(I)-MCM-41 (referenced against neat MCM-41). (c2) Difference FT-IR upon exposure to 1 atm of O₂ gas for 24 h in the dark. (d) Difference FT-IR spectra after photolysis (355 nm, 165 mW cm⁻¹, 2.5 h) of the CO₂-loaded (1 atm) ZrCu(I)-MCM-41.

revealed by optical difference spectroscopy following exposure of the ZrCu(I) sieve to 1 atm of O₂ gas at room temperature, shown in Figure 1b; the rise of the Cu(II) d–d band at 800 nm¹⁶ is accompanied by absorbance loss in the 300–500 nm region. Since neither Cu(I) nor Zr(IV) possesses ligand field transitions or a LMCT band in this spectral region, the absorbance loss can only originate from a MMCT transition Zr(IV)/Cu(I) → Zr(III)/Cu(II). No such absorbance loss in the 300–500 nm region was detected when monometallic Cu(I)-MCM-41 was exposed to an O₂ atmosphere; only the growth of the Cu(II) band was observed in that case.¹³

The key information on the structure of the bimetallic site was furnished by the low-frequency metal–oxygen stretching modes. The FT-IR spectrum features a broad absorption at 930 cm⁻¹ typical for Si–O stretching vibrations of SiO bonds adjacent to a metal center.¹¹ More interestingly, a Cu(I)–O stretch absorption is observed around 650 cm⁻¹ (Figure 1c). When the Cu(I) precursor was grafted onto a Zr-MCM-41 sample featuring Zr–¹⁸OH and Si–¹⁸OH groups,¹⁷ the band showed a red shift of 30 cm⁻¹ characteristic for a Cu–O mode. Upon exposure of the ZrCu(I)-MCM-41 material to an O₂ atmosphere, the ν(Cu(I)–O) absorption decreased under concurrent growth of a band around 540 cm⁻¹ (Figure 1c). Closer inspection of the depletion spectrum upon

The observed CO and H₂O products, with the oxygen of water originating from CO₂, point to dissociation of carbon dioxide upon capture of an electron from an MMCT-excited Zr center. The transient O⁻ so produced will pick up a proton from a surface silanol group (approximately three SiOH groups per square nanometer).²⁰ The surface OH radical, like the CO product, will diffuse through



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