Communication

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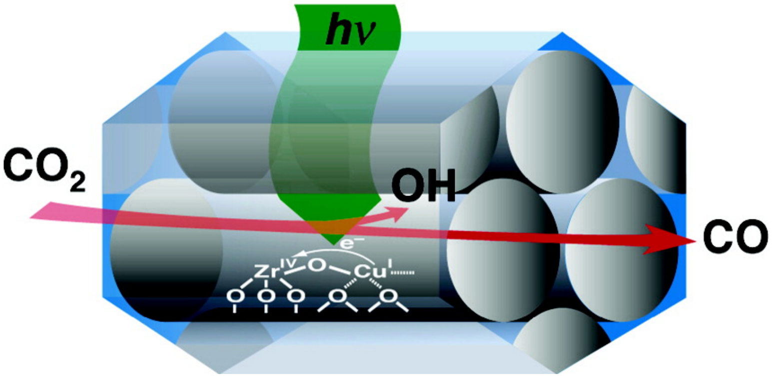

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Photochemical CO_2 Splitting by Metal-to-Metal Charge-Transfer Excitation in Mesoporous ZrCu(I)-MCM-41 Silicate Sieve

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The photoreduction of CO_2 by H_2O 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 TiO_2, $SrTiO_3$, 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 O_2 (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 CO_2 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 CO_2 reduction by H_2O 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 CO_2 by H_2O at substantially better efficiency than dense-phase TiO_2 particles.[9] Prolonged photolysis gave CH_3OH and CH_4 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 O_2 are the initial single-photon redox products.[10] Use of isolated tetrahedral Ti centers on nanoporous support is a promising development for CO_2 photoreduction by H_2O, 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 CO_2 to CO. The site consists of Zr(IV) oxo-bridged to Cu(I), covalently anchored on the pore surface of MCM-41 sieve.

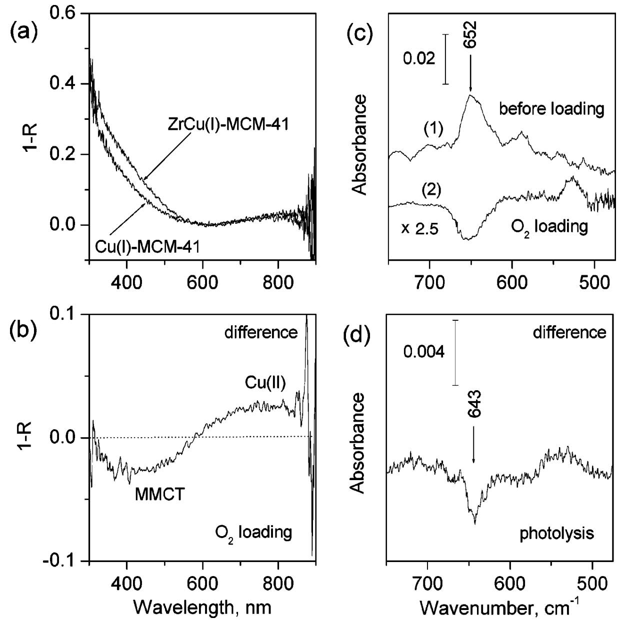

Figure 1. (a) UV−vis DRS of ZrCu(I)-MCM-41 and Cu(I)-MCM-41. (b) Difference DRS spectra recorded after and before exposure of ZrCu(I)-MCM-41 to O_2 gas (1 atm) at room temperature for 8 h. (c1) FT-IR spectrum of ZrCu(I)-MCM-41 (referenced against neat MCM-41). (c2) Difference FT-IR upon exposure to 1 atm of O_2 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 CO_2-loaded (1 atm) ZrCu(I)-MCM-41.

Assembly of covalently anchored ZrCu(I) moieties on the MCM-41 pore surface was accomplished by first grafting tetrahedral Zr centers using the established $ZrCp_2Cl_2$ 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 $Cu^I(NCCH_3)_4PF_6$ in 100 mL of CH_2Cl_2 (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 CH_3CN 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 revealed by optical difference spectroscopy following exposure of the ZrCu(I) sieve to 1 atm of O_2 gas at room temperature, shown in Figure 1b; the rise of the Cu(II) d−d band at 800 nm[16] 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 O_2 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−^{18}OH and Si−^{18}OH 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 O_2 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

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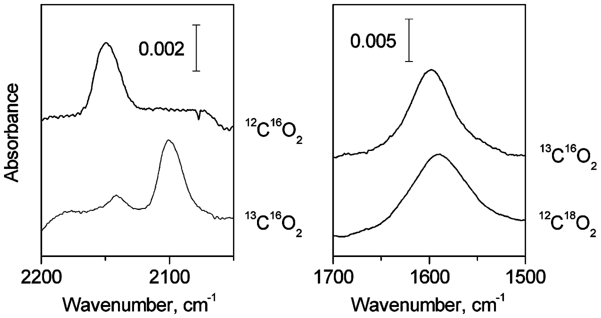
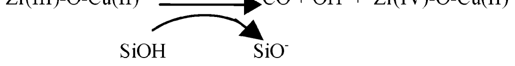


Figure 2. FT-IR spectra recorded before and after irradiation of ZrCu(I)-MCM-41 loaded with 1 atm of CO_2, $^{13}CO_2$, or $C^{18}O_2$ at 355 nm (110 mW cm^{-2}) for 2.5 h.

oxidation by O_2 shows a shoulder at the low-frequency side of the ν(Cu(I)−O) stretch. On the other hand, depletion of ν(Cu(I)−O) upon photoreduction of CO_2 (see discussion below) occurs exclusively at 643 cm^{-1}, with accompanying ν(Cu(II)−O) growth at 540 cm^{-1} (Figure 1d). Since MMCT-induced photolysis results only in the oxidation of Cu(I) centers that are part of an MMCT site, this indicates that the 643 cm^{-1} component of the ν(Cu(I)−O) profile originates from a Cu(I)−O−Zr bridge. A similar Cu(I)−O band was observed when the $Cu^I(NCCH_3)_4^+$ complex was grafted onto porous ZrO_2 (Aldrich).[13] The absorption at 650 cm^{-1} and higher is mainly due to Cu(I)−O−Si linkages of isolated Cu centers. We conclude that the inorganic MMCT moiety features an oxo bridge.[18]

When 750 Torr CO_2 gas was loaded into ZrCu(I)-MCM-41 sieve and the Zr−O−Cu(I) MMCT chromophore irradiated at 355 nm, infrared growth was detected at 2148 and at 1600 cm^{-1}, as shown in Figure 2. Adsorption of an authentic sample of CO gas on the sieve confirmed the assignment of the 2148 cm^{-1} band to carbon monoxide bound to Cu(I). When the photoreaction was conducted with $^{13}CO_2$ or $C^{18}O_2$, the corresponding labeled product ^{13}CO (2101 cm^{-1}) or $C^{18}O$ (2096 cm^{-1}) was observed. No growth of isotopically labeled CO was detected when a ZrCu−MCM-41 sieve was used with Cu in the oxidized Cu(II) state. These observations prove that the carbon monoxide originates from the MMCT-induced photoreduction of CO_2. The concurrent intensity loss of the Cu(I)−O−Zr mode at 643 cm^{-1} (Figure 1d) confirms that the carbon dioxide photoreduction is accompanied by the oxidation of Cu(I) linked to the Zr center. Photoreduction of $C^{18}O_2$ leads to growth of $H_2{}^{18}O$ at 1594 cm^{-1} (Figure 2), indicating that the oxygen atom of water stems from CO_2.[19] When the CO_2 photoreduction was attempted in TiCu(I)-MCM-41, whose MMCT absorption is much more intense,[11] no significant CO growth was detected. This is consistent with the substantially lower reducing power of transient Ti^{3+} compared to Zr^{3+}.

The observed CO and H_2O products, with the oxygen of water originating from CO_2, 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 the pores until trapped and reduced to H_2O at an isolated Cu(I) site. Hence, the proposed mechanism is CO_2 splitting at the excited MMCT sites, consistent with the reaction path of single UV photon-induced CO_2 reduction by H_2O to CO and O_2 in framework TiMCM-41 sieve.[10] This is the first observation of CO_2 photoreduction at a binuclear MMCT site at the gas−solid interface. If a metal M can be identified that oxidizes H_2O by visible light-induced LMCT, thereby reducing the bimetallic moiety to its original state, a Z-scheme for CO_2 reduction by H_2O under visible light can be envisioned.



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Supporting Information Available: UV−vis, FT−Raman, and FT−IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) The focus here is on the photoreduction of CO_2 with H_2O acting as the direct electron donor, rather than photochemical generation of H_2 from water followed by dark thermal hydrogenation of carbon dioxide.

(3) Carbon dioxide photoreduction under UV light at semiconductor materials (mainly to CO) using donors other than H_2O has been studied. Typical donors used are Cu metal particles[4a,b] or Cu_2O.[4c] UV light-induced dissociation of CO_2 to CO at excited Rh carbonyl complexes on alumina support has also been reported.[4d]

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(13) Spectra shown in Supporting Information.

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(17) Residual Cp ligands of anchored Zr centers were replaced by Zr−^{18}OH through heating in an $^{18}O_2$ atmosphere at 550 °C. The long calcination period needed (5 h) resulted in ^{18}O exchange of silanol groups as well, as indicated by the Si−^{18}OH stretch at 3735 cm^{-1}.

(18) FT-Raman spectra of the ZrCu(I)-MCM-41 sieve did not show the characteristic absorptions of particles or clusters of Cu_2O (190, 154 cm^{-1}), CuO (348, 299 cm^{-1}).[13] In particular, comparison of the noise level of the ZrCu(I)-MCM-41 Raman spectrum with the intensity of the 190 cm^{-1} peak of a mechanical mixture of Cu_2O and MCM-41 allowed us to conclude that at most 10%, if any, of the Cu present in ZrCu(I) or Cu(I) sieve is engaged in Cu_2O cluster formation.

(19) Observation of the H_2O bending mode of water coordinated to Cu(II) at 1600 cm^{-1} is consistent with literature data on model complexes, e.g., see: Bushiri, M. J.; Nayar, V. U. *Spectrochim. Acta A* **2002**, *58*, 899−909.

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