Steven L. Suib Editor





New and Future Developments in Catalysis

Activation of Carbon Dioxide

NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

ACTIVATION OF CARBON DIOXIDE

Edited by

Steven L. Suib

Department of Chemistry and Chemical Engineering and Institute of Materials Science, The University of Connecticut, Storrs, CT 06269-3060



AMSTERDAM • BOSTON • HEIDELBERG • LONDON NEW YORK • OXFORD • PARIS • SAN DIEGO SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO Elsevier Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK 225 Wyman Street, Waltham, MA 02451, USA

Copyright © 2013 Elsevier B.V. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher.

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at http://elsevier.com/locate/permissions, and selecting Obtaining permission to use Elsevier material.

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress.

ISBN: 978-0-444-53882-6

For information on all Elsevier publications visit our web site at store.elsevier.com

Printed and bound in Poland 13 14 15 16 17 10 9 8 7 6 5 4 3 2 1



20

Photocatalytic Conversion of Carbon Dioxide into Fuels Using Layered Double Hydroxides Coupled with Hydrogen or Water

Naveed Ahmed, Motoharu Morikawa, and Yasuo Izumi

Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

20.1 INTRODUCTION

Carbon dioxide is one of the major greenhouse gases. Several methods for reducing atmospheric CO_2 concentration have been investigated, such as increasing green carbon sinks (plants, phytoplankton, and algae containing chloroplasts); increasing dissolved carbonate and its salts in sea water; or capturing CO_2 with transfer to the bottom of the sea in a supercritical state [1]. The global strategy for the suppression of CO_2 emission based on Kyoto Protocol is not on the right track due to conflicting interests between developed and developing countries and the uncertainty of an energy paradigm shift from fossil fuels to clean energy. At present, the contribution of nuclear power is unstable due to the question of safety whereas the contribution of natural energy (biomass, hydropower, solar, wind, and geothermal energy) to total energy consumption has been growing much slower than expected [2]. Thus, it is urgently important to investigate sustainable natural energy.

As one of the options of natural energy, it is advantageous to capture CO_2 produced from human activity and from the atmosphere and convert this gas to fuels using sustainable

20. PHOTOCATALYTIC CONVERSION OF CARBON DIOXIDE INTO FUELS

sunlight, because this option solves the problems of global warming and sustainable energy shortage simultaneously. Semiconductor-type photocatalysts are hopeful because they can be cheaper by choosing inexpensive elements in comparison to metal complex homogenous-phase photocatalysts consisting of precious noble metals [3]. Some good reviews for CO_2 photoreduction have been reported focusing on TiO₂-based photocatalysts [4], on the possibility of solar fuel [5], and nanocomposite photocatalysts [6]. But the number of publications of photoreduction of CO_2 is growing even rapidly later than 2010 and newer reviews are needed. In this chapter, recent works for semiconductor-type photocatalysts to reduce CO_2 are reviewed.

20.2 CO₂ PHOTOREDUCTION WITH WATER USING METAL OXIDE AND OTHER SEMICONDUCTOR-TYPE PHOTOCATALYSTS

The photoreduction of CO₂ follows a reduction to carbon monoxide or a consecutive reaction to organic compounds as below:

$$CO_2 \xrightarrow{2e^-} CO,$$

$$CO_2 \xrightarrow{2e^-} HCO_2 H \xrightarrow{2e^-} HCHO \xrightarrow{2e^-} CH_3 OH \xrightarrow{2e^-} CH_4.$$

In contrast to most homogeneous photocatalysts that produce CO with the help of sacrificial reducing agents, e.g., alkyl amines and alcohols [6,7], various products ranging from two-electron-reduced formic acid and CO to eight-electron-reduced methane were produced using semiconductor photocatalysts often without the help of sacrificial reductant [4,8]. The reasons why the selectivity to each product was determined and how multiple-electron photoreduction proceeds are not fully known [9].

In the absence of reducing agent, the photoreduction of CO_2 to CO is a combination of water oxidation reaction and CO_2 reduction reaction:

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2,$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O.$$

CO was reported as a minor product in addition to major methane formation using semiconductor photocatalysts, TiO_2 [10,11], and ZrO_2 [10] (Table 20.1A).

The photocatalytic production of formic acid was reported using TiO₂ under supercritical CO₂ [12,13]. The CO₂ pressure of supercritical condition was reduced from 6.5 to 9.0MPa, and then pure water or acidic solution was added to the reactor. In particular, formic acid was preferably formed ($1.8 \mu mol h^{-1} g_{cat}^{-1}$) when acidic solution was added as a proton source (Table 20.1B) [13].

The photocatalytic formation (and detection) of formaldehyde has been reported very rarely mostly because of the instability of formaldehyde. In spite of this problem, pioneering work for photocatalysts reported formaldehyde formation using various semiconductors with the formation rate order: $CdS>ZnO\sim TiO_2>GaP\sim SiC$ [14] (Table 20.1C).

Photocatalytic conversion of CO_2 into methanol in aqueous solution was reported in several papers, but care should be taken for the possibility that the C source of produced methanol was not CO_2 but impurity C species accumulated during the catalyst preparation, typically derived from alkyl groups of precursor compounds. The reaction pathway to CO_2 was

Photocatalysts	Formation RatesReactantsLight $(\mu \mod h^{-1} g_{cat}^{-1})$		Formation Rates (μ mol h ⁻¹ g ⁻¹ _{cat})	References	
(A) Product: CO					
TiO ₂	$CO_2(5\%) + H_2O(g, 95\%)$	LP Hg	0.11	[10]	
ZrO_2	$CO_2(5\%) + H_2O(g, 95\%)$	LP Hg	0.045	[10]	
TiO ₂	$CO_2(sat) + H_2O(l)$	HP Hg arc	0.35	[11]	
(B) Product: HCO ₂ H					
TiO ₂ (anatase)	CO ₂ (6.5 MPa), H ₂ O(l)	Xe	1.0	[12]	
TiO ₂ (anatase)	CO ₂ (9.0 MPa), H ₂ O(l)	Xe	1.8	[13]	
(C) Product: HCHO					
CdS	$CO_2(saturated) + H_2O(l)$	Xe/HP Hg	29	[14]	
ZnO	$CO_2(saturated) + H_2O(l)$	Xe/HP Hg	17	[14]	
TiO ₂	$CO_2(saturated) + H_2O(l)$	Xe/HP Hg	16	[14]	
GaP	$CO_2(saturated) + H_2O(l)$	Xe/HP Hg	14	[14]	
SiC	$CO_2(saturated) + H_2O(l)$	Xe/HP Hg	14	[14]	
(D) Product: CH ₃ OH					
Ti-Y-zeolite	$CO_2(24 \mu mol) + moisture$ (120 μmol)	HP Hg	0.031	[16]	
Ti-MCM-48	$CO_2(24 \mu mol) + moisture$ (120 μmol)	HP Hg	3.1	[17]	
Ti-SBA-15	$CO_2(36 \mu mol) + moisture$ (180 μmol)	HP Hg	0.081	[18]	
$TiO_2(d=14 nm)$	CO ₂ (saturated) + 0.2 N NaOH	Hg	0.047	[19]	
Ag-TiO ₂	CO ₂ (saturated) + 0.2 N NaOH	Hg	0.094	[20]	
(E) Product: CH ₄					
TiO ₂ (JRC-TIO-4)	CO_2 + moisture (111 kPa)	UV	0.014	[21]	
Ti–Y-zeolite	$CO_2(24 \mu mol) + moisture$ (120 μmol)	HP Hg	0.046	[16]	
Ti-MCM-48	$CO_2(24 \mu mol) + moisture$ (120 μmol)	HP Hg	7.5	[17]	
Ti-SBA-15	$CO_2(36 \mu mol) + moisture$ (180 μmol)	HP Hg	0.31	[18]	
Ti-FSM-16	$\begin{array}{c} CO_2(36\mu mol) + moisture \\ (180\mu mol) \end{array}$	HP Hg	0.15	[22]	
Ti–porous SiO ₂ film	$CO_2(36 \mu mol) + moisture$ (180 μmol)	HP Hg	0.084	[23]	

TABLE 20.1	Photocatalytic Reduction	of CO_2 with	Water usir	ng Metal	Oxide and	other S	Semiconduct	tor-
Type Photocat	alysts							

20. PHOTOCATALYTIC CONVERSION OF CARBON DIOXIDE INTO FUELS

monitored by Fourier-transform infrared (FTIR) spectroscopy [15] and kinetic study for thoroughly washed TiO_2 (P25, Degussa) samples [11]. CO was mainly produced instead of methane or methanol in the CO₂ photoreduction test using thoroughly washed TiO_2 (P25) with an Hg lamp (Table 20.1A).

For the mixture of CO_2 gas and moisture, methanol was formed using atomically dispersed Ti species on molecular sieves (Ti–Y-zeolite, Ti–MCM-48, and Ti–SBA-15) with UV-visible light [16–18] (Table 20.1D), but the major product was methane in these reports (Table 20.1E). The average particle size of 14 nm was optimized for TiO₂ for the photoreduction of CO₂ to methanol [19]. The additive effects of metal nanoparticles on photocatalytic methanol formation were also reported [20].

TiO₂ has been most frequently reported for the photoreduction of CO₂ to produce methane. TiO₂ consisting of major anatase phase and minor rutile phase formed methane very slowly (0.014 μ mol h⁻¹ g⁻¹_{cat}) [21]. The photocatalytic activity per unit amount of Ti was significantly enhanced when Ti oxide species were anchored within the pores of zeolite [16], ordered mesoporous SiO₂ [22], and porous SiO₂ thin films [23], but the activity per unit amount of catalyst modestly increased because the dispersion of Ti site increased [16–18,22,23] (Table 20.1E). Promoting effects of CdSe and Pt were discussed for the photocatalytic CO₂ reduction into methane [24].

In summary, semiconductors, typically TiO₂, were active for CO₂ photoreduction in water. The photocatalytic rates using anatase/rutile-type TiO₂ were mostly less than 1 μ mol h⁻¹ $g_{cat'}^{-1}$ but the photoactivity was increased to 1 – 10 μ mol h⁻¹ g_{cat}^{-1} by dispersing Ti sites on molecular sieves, by the addition of promoters, e.g., CdSe and Pt, and under supercritical reaction conditions.

20.3 CO₂ PHOTOREDUCTION WITH HYDROGEN USING METAL OXIDE-BASED AND OTHER SEMICONDUCTOR-TYPE PHOTOCATALYSTS

The photoreduction of CO_2 using hydrogen is an alternative option to reduce the amount of CO_2 sustainably, if the hydrogen was produced using a sustainable energy source, e.g., water splitting using sunlight [1].

The photoreduction of CO₂ using hydrogen as a reductant has been reported to produce CO using Rh/TiO₂ (5.1 μ mol h⁻¹ g_{cat}⁻¹) [25], ZrO₂ (0.56–0.62 μ mol h⁻¹ g_{cat}⁻¹) [10,26], MgO (1.6 μ mol h⁻¹ g_{cat}⁻¹) [27], and β -Ga₂O₃ (0.76 μ mol h⁻¹ g_{cat}⁻¹) [28], and to produce methane using Ti–SBA-15 (0.012 μ mol h⁻¹ g_{cat}⁻¹) [29] (Table 20.2). Thus, metal oxide semiconductors, e.g., TiO₂, ZrO₂, MgO, and Ga₂O₃, photoreduced CO₂ in the presence of H₂ at the rate of ~1 μ mol h⁻¹ g_{cat}⁻¹. Rhodium was an effective promoter.

20.4 SYNTHESES AND CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES FOR CO₂ PHOTOREDUCTION WITH HYDROGEN

Layered double hydroxide (LDH) compounds are a family of clay-like materials. Their layers are positively charged in contrast to clay families in which the layers are negatively charged

20.4 synthesis and characterzation of layered double hydroxides for co_2 photoreduction 593

				Formation Rates			
Photocatalysts	CO ₂	H_2	Light	$(\mu mol h^{-1} g_{cat}^{-1})$	References		
(A) Product: CO							
Rh/TiO ₂	150 µmol	50 µmol	HP Hg	5.1	[25]		
ZrO_2	150 µmol	50 µmol	HP Hg	0.56	[26]		
ZrO_2	5.6 kPa	106 kPa	UV	0.62	[10]		
MgO	150 µmol	50 µmol	HP Hg	1.6	[27]		
β -Ga ₂ O ₃	$150\mu mol$	50 µmol	HP Hg	0.76	[28]		
(B) Product: CH ₄							
Ti-SBA-15	38µmol	76 µmol	HP Hg	0.012	[29]		

TABLE 20.2 Photocatalytic Reduction of CO_2 with Molecular Hydrogen Using Metal Oxide and OtherSemiconductor-type Photocatalysts

[1,30–32]. LDHs are the materials based on the layered structure of brucite Mg(OH)₂, which has a hexagonal crystal structure and in which the MgO₆ octahedra are linked at the edge to form sheets. The charge of cationic sheets formulated as $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}$ is compensated with an intercalated anion group, e.g., CO_3^{2-} , SO_4^{2-} , NO_3^{-} , CI^- , or OH⁻. The M^{II} site can be Mg, Mn, Fe, Co, Ni, Cu, or Zn and the M^{III} site can be Al, Cr, Mn, Fe, or Ga. The value of *x* varies normally within the range of 0.17–0.33. The molar amount of structural water intercalated between the cationic layers is about a half of the total molar amount of metal cations.

Ordered LDHs consisting of zinc and/or copper hydroxides were reportedly combined with gallium. The interlayer anions were carbonates or $[Cu(OH)_4]^{2-}$ [33]. The BET surface area (S_{BET}) values were in the range between 83 and $35 \text{ m}^2 \text{ g}^{-1}$ (Table 20.3). The S_{BET} value for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ was 23% greater than that for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$. The S_{BET} values for $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ decreased by 50% compared to the value for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ because of the substitution of carbonate ions with $[Cu(OH)_4]^{2-}$ ions. On the other hand, when compared with the S_{BET} value for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$, the values for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ did not change significantly (+8.8%).

The X-ray diffraction (XRD) (003), (006), (009), (104), (015), (107), (018), (1010), (0111), (110), (113), and (116) peaks were observed for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (Figure 20.1a) [34,35]. There was a downward shift in these peaks for $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (b) and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (d). Weaker peaks derived from the CuO (+ mark) and Cu(OH)₂ impurity phase (*mark) appeared in the spectra of $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (Figure 20.1b and d). Diffraction peaks due to impurity phases were not found for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (a) and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (c).

The interlayer interval was 0.751 and 0.753 nm on the basis of the (003) diffraction angle for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (Table 20.3A and B) [30]. The interlayer interval increased from 0.751 nm for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ to 0.792 nm for $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (Table 20.3A and C), reflecting the

				E _g (eV)				Interlattice	
		_		Fit to $\alpha \times hv \propto (hv - E_g)^n$		Distance (nm)			
Entry	Sample	S_{BET} (m ² g ⁻¹)	Extrapolated	$n = \frac{1}{2}$	$\frac{3}{2}$	2	3	(0 0 3)	
A	$[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$	70 ^a (83 ^b)	5.6	5.9	5.4	5.2	5.0	0.751	
В	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$	57 ^a (67 ^b)	3.5	4.2	3.2	3.0	2.6	0.753	
С	$[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-}\cdot mH_2O$	35 ^a	4.2	4.8	3.6	3.4	2.7	0.792	
	(impurity phase(s))		3.2	4.6	3.0	2.8	2.5		
D	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-}\cdot \textit{mH2O}$	62 ^a	3.0	3.2	2.8	2.7	2.6	0.782	

TABLE 20.3 Physicochemical Characterization of $[Zn_{3-x}Cu_xGa(OH)_8]_2^+[A]^{2-} \cdot mH_2O$ (x=0, 1.5; A=CO₃, Cu(OH)₄) LDHs

^aPreheated at 383 K for 2h under vacuum. ^bPreheated at 423 K for 1h under vacuum.



FIGURE 20.1 XRD spectra of as-synthesized samples of $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (a), $[Zn_3Ga(OH)_8]_2^+$ $[Cu(OH)_4]^{2-} \cdot mH_2O$ (b), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (c), and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+$ [Cu(OH)₄]²⁻ $\cdot mH_2O$ (d). (*) and (+) marks indicate peaks derived from Cu(OH)₂ and CuO powders, respectively.

greater size of $[Cu(OH)_4]^{2-}$ ions when compared to that of $(CO_3)^{2-}$ [36,37]. In a similar manner, by substituting $(CO_3)^{2-}$ with $[Cu(OH)_4]^{2-}$, the interlayer interval increased from 0.753 nm for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+$ (CO_3)²⁻ · *m*H₂O to 0.782 nm (Table 20.3B and D).

In the UV-visible absorption spectra for LDH compounds (Figure 20.2), the E_g values for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O_{and} [Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O_{error} = 5.6$ and 4.2 eV, respectively (Table 20.3A and C). Based on the corresponding *n* value (1/2 or 3/2) by the fitting to the Davis-Mott equation, the electronic transition was direct from oxygen 2p to Cu 3d, 4s, or 4p levels and Zn/Ga 4s or 4p levels for $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ and $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$. In addition, a shoulder peak corresponded to E_g values of 3.2 eV for $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (Figure 20.2b) originated from the Cu(OH)_2 and/or CuO impurity phase(s) that was evident in XRD pattern (Figure 20.1b). By fitting to the Davis-Mott equation (n = 3/2; Table 20.3C), the electronic transition was forbidden direct



FIGURE 20.2 Diffuse reflectance UV-visible absorption spectra of as-synthesized samples of $[Zn_3Ga(OH)_8]_2^+$ $(CO_3)^{2-} \cdot mH_2O$ (a), $[Zn_3Ga(OH)_8]_2^+ [Cu(OH)_4]^{2-} \cdot mH_2O$ (b), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+ (CO_3)^{2-} \cdot mH_2O$ (c), and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+ [Cu(OH)_4]^{2-} \cdot mH_2O$ (d).

from oxygen 2p to Cu 3d, 4s, or 4p levels of Cu(OH)₂ and/or CuO phase(s). The UV absorption edge shifted toward the lower energy side for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ (Figure 20.2c) when compared to $[Zn_3Ga(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ (a). The E_g value was 3.5 eV (Table 20.3B). Upon further replacing interlayer (CO₃)²⁻ ions with $[Cu(OH)_4]^{2-}$ ions, the band gap further decreased to 3.0 eV (Table 20.3D). This band-gap value corresponds to the boundary wavelength between UV and visible light.

Based on the Cu K-edge extended X-ray absorption fine structure (EXAFS) spectrum for the LDH sample of $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (Figure 20.3), two intense peaks in the Fourier transform at 0.16 and 0.27 nm (phase shift uncorrected) derived from Cu—O and Cu ... Zn (or Cu ... Ga) pairs, respectively, appeared, but a peak derived from Cu—Cl bond(s) at ~0.195 nm [38] (phase shift uncorrected) was not present (Figure 20.3b). No Cu—Cl peaks



FIGURE 20.3 Cu K-edge EXAFS spectra for $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^2 \cdot mH_2O$ sample. (a) k^3 -weighted EXAFS χ -function and (b) its associated Fourier transform. The solid and dotted lines represent the magnitude and the imaginary part in (b).



FIGURE 20.4 Model structure of $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ based on XANES and EXAFS analyses.

were found in the Fourier transform for this LDH photocatalyst, demonstrating the complete hydrolysis of $[CuCl_4]^{2-}$ into $[Cu(OH)_4]^{2-}$ during the synthesis:

$$[CuCl_4]^{2-} + 4NaOH \rightarrow [Cu(OH)_4]^{2-} + 4NaCl.$$
 (1)

$$2[Zn_{3}Ga(OH)_{8}]^{+} + [Cu(OH)_{4}]^{2-} + mH_{2}O \rightleftharpoons [Zn_{3}Ga(OH)_{8}]^{+}_{2}[Cu(OH)_{4}]^{2-} \cdot mH_{2}O.$$
(2)

Based on the Cu K-edge X-ray absorption near-edge structure (XANES) spectra and the theoretical simulation, complex formation between cationic layer and $[Cu(OH)_4]^{2-}$ anion was suggested [39] (Figure 20.4):

$$[Zn_{3}Ga(OH)_{8}]_{2}^{+}[Cu(OH)_{4}]^{2-} \cdot mH_{2}O \rightleftharpoons Zn_{6}Ga_{2}(OH)_{13}\{(\mu-O)_{3}Cu(OH)\} \cdot mH_{2}O + 3H_{2}O. (3)$$

20.5 CO₂ PHOTOREDUCTION WITH HYDROGEN USING LAYERED DOUBLE HYDROXIDES

LDH photocatalysts were reported to produce not only CO but methanol in the CO₂ photoreduction with hydrogen. While $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ was CO selective (61 mol%), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ was methanol selective (68 mol%; Figure 20.5a, b and Table 20.4A, B).

When $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ was preheated at 423K (Figure 20.5d), the methanol formation rate increased by a factor of 1.8 (0.31 µmol h⁻¹ g_{cat}^{-1}). Due to the preheating at 423K, the S_{BET} value for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ increased by 18%, but the increase did not fully explain the increase of photocatalytic methanol and CO formation by a factor of 1.8 and 2.3, respectively (Table 20.4D). The available interlayer space that was

		Formation rate (μ mol h ⁻¹ g _{cat} ⁻¹				Selectivity
Entry	Photocatalyst	CH ₃ OH	СО	Σ	(%, C-base)	(mol%)
A	$[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$	0.051	0.080	0.13	0.02	39
		(± 0.004)	(±0.006)			(±4)
В	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-}\cdot \mathit{m}H_2O$	0.17	0.079	0.25	0.03	68
		(±0.014)	(±0.006)			(±4)
С	$[Zn_{3}Ga(OH)_{8}]_{2}^{+}(CO_{3})^{2-}\cdot \textit{m}H_{2}O^{b}$	0.050	0.074	0.12	0.02	40
		(±0.004)	(±0.006)			(±4)
D	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-}\cdot \mathit{m}H_2O^\flat$	0.31	0.18	0.50	0.07	63
		(±0.009)	(±0.002)			(±1)
Е	$[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$	0.30	0.13	0.43	0.04	71
		(±0.009)	(±0.010)			(±2)
F	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$	0.49	0.070	0.56	0.05	88
		(± 0.015)	(±0.006)			(±2)

TABLE 20.4 Rates of Photocatalytic Conversion of CO_2 with H_2 into CH_3OH and CO Over LDH Photocatalysts^a

^aThe catalyst amount was 100 mg. 2.3 kPa of CO₂ and 21.7 kPa of H₂. Values in the parentheses are experimental errors for evaluation. ^bPreheated at 423 K for 1 h under vacuum.



FIGURE 20.5 Time course of photocatalytic reactions in CO₂ (2.3kPa) + H₂ (21.7kPa). Hundred milligram of the LDH catalyst was charged: fresh $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (a), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (b), $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ preheated at 423K (c), $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ preheated at 423K (d), fresh $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (e), and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (f). The reactor was illuminated from a 500-W Xe arc lamp. CO₂ (\Box ; diamond), H₂O (\blacktriangle ; triangle), CH₃OH (\blacksquare ; square), and CO (\bullet ; circle).

created at 423 K should facilitate the diffusion of CO₂ into the reaction space and the reaction with the surface hydroxy groups that are bound to the Cu sites.

By switching the interlayer anion group from carbonate to $[Cu(OH)_4]^{2-}$ for LDH compounds consisting of $[Zn_3Ga(OH)_8]^+$ cations, the methanol formation rate increased by a factor of 5.9 (Table 20.4E and A) while the methanol selectivity did not change (71–68 mol%). By the substitution of anions, the S_{BET} values even decreased by 50% (Section 20.4). For the $[Zn_{1.5}Gu(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$, the formation rates of methanol and CO for specific quantities of Cu were 0.051 and 0.024 µmol h⁻¹ mmol_{Cu'}^{-1} respectively. These values increased to 0.097 and 0.056 µmol h⁻¹ mmol_{Cu'}^{-1} respectively, when preheated at 423 K in a vacuum. For the $[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$, the formation rates of methanol and CO were 0.30 and 0.13 µmol h⁻¹ mmol_{Cu'}^{-1} respectively. Therefore, the interlayer Cu sites were 5.3–5.9 times more effective than Cu sites in cationic layers, if we assume that the Cu atoms are primary active sites.

Using $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (Figure 20.4f), the methanol formation rate and selectivity further increased to 0.49 µmol h⁻¹ g_{cat}⁻¹ and 88 mol% (Table 20.4F). The methanol formation rate per unit amount of Cu was 0.12 µmol h⁻¹ mmol_{Cu}⁻¹ (Table 20.5F), which is in close agreement with the calculated value of 0.11 µmol h⁻¹ mmol_{Cu}⁻¹, which was contributed by the in-layer Cu sites (3/4 × 0.051 µmol h⁻¹ mmol_{Cu}⁻¹) and the interlayer Cu sites (1/4 × 0.30 µmolh⁻¹ mmol_{Cu}⁻¹). The steric availability (accessibility) of {(µ–O)₃Cu(OH)} sites (Figure 20.4) may be related to the reactivity difference.

In this context, the Cu site plays a photocatalytic role by binding CO₂ and coupling CO₂ with protons and photogenerated electrons, utilizing the Cu^I and Cu^{II} redox couple [1,33]. This binding between CO₂ and Cu was spectroscopically monitored in the multiple scattering region of Cu K-edge XANES for $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$. The binding suggested the reaction mechanism via the CO₂ insertion to hydroxy group to form hydrogen carbonate (Scheme 20.1a \rightarrow b). The one-electron reduction steps b \rightarrow c \rightarrow d in Scheme 20.1 should be promoted utilizing the Cu^{II} and Cu^{II} redox couple. Subsequent one-electron reduction steps e \rightarrow f, f \rightarrow g, and g \rightarrow h should also be coupled with the Cu^{II} and Cu^{II} redox. Final one-electron reduction in the step h \rightarrow a produces methanol. If the species e is dehydrated, another catalytic reaction cycle to form CO is proposed regenerating species a. The role of the Cu^{II} sites was also suggested in the CO₂ photoreduction in alkaline aqueous solution [40].

The photocatalytic energetic diagram is depicted in Scheme 20.2. The band-gap values (5.6–3.5eV) for $[Zn_3Ga(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$

TABLE 20.5 Rates of Photocatalytic Formation of CH_3OH and CO per the Quantity of Cu in the LDHPhotocatalysts^a

		Formation Rate Per Amount of $Cu (mmol h^{-1}mmol_{Cu}^{-1})$			
Entry	Photocatalyst	CH ₃ OH	СО	Σ	
В	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-}\cdot \mathit{m}H_2O$	0.051	0.024	0.077	
D	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-}\cdot \mathit{m}H_2O^{\mathrm{b}}$	0.097	0.056	0.15	
Е	$[Zn_3Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$	0.30	0.13	0.43	
F	$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-}\cdot mH_2O$	0.12	0.017	0.14	

^aThe catalyst amount was 100 mg. Values in the parentheses are experimental errors for evaluation. ^bPreheated at 423 K for 1 h under vacuum.



SCHEME 20.1 Proposed photocatalytic catalytic cycle of CO₂ reduction to methanol or CO over Zn–Cu–Ga LDH catalysts.



SCHEME 20.2 Energy levels at the band gap for ZnO, $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$, and $[Zn_3Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ versus the reaction potentials for each step of CO₂ reduction to methanol/CO and H₂ oxidation to protons.

were greater than that for ZnO (3.2 eV), enabling the CO₂ photoreduction at relatively higher potentials at -0.32 V to form methanol and to form CO at -0.11 V by supplying photoexcited electrons in conduction band to CO₂. In Scheme 20.2, the center of the conduction band minimum energy and the valence band top energy was assumed to be constant, but these energy levels should be exactly determined later. On the other hand, photogenerated holes at the valence band were neutralized with electrons formed in the H₂ oxidation (0V). The selectivity to produce methanol *versus* CO formation increased by adding Cu to [Zn₃Ga(OH)₈]⁺₂(CO₃)²⁻ · *m*H₂O (Table 20.4). The band gap became narrower with the addition of Cu; however, the potential for the methanol formation step (CO₂+6H⁺+6e⁻ → CH₃OH+H₂O) [24] was 0.21 V higher than that for the CO formation step (Scheme 20.2). Thus, the selectivity of CO₂ photoreduction was not controlled by energetics of reaction steps in the viewpoint of electron flow [41–45], but the adsorption of CO₂ and the stability of the reduced species is critical [1].

The durability of LDH catalysts and the verification of photocatalytic reaction mechanism were also reported. When the $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^2 \cdot mH_2O$ photocatalyst was



FIGURE 20.6 Time course of photoreactions in CO₂ (2.3 kPa) + H₂ (21.7 kPa) using 100 mg of $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+$ (CO₃)²⁻ · mH₂O for 20h. Other reaction conditions and legends are the same as those for Figure 20.4.



FIGURE 20.7 Time course of photocatalytic reaction in CO $(2.3 \text{ kPa}) + H_2 (21.7 \text{ kPa})$. 0.10g of the LDH photocatalysts $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ (a1, a2) and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ (b1, b2) was charged. The reactor was at 313K without Xe arc lamp irradiation (a1, b1) while it was at 313K under UV-visible light from a Xe arc lamp (a2, b2). CO₂ (\Box ; diamond), H_2O (\blacktriangle ; triangle), CH₃OH (\blacksquare ; square), and CO (\bullet ; circle).

tested for 20h illuminated with UV-visible light, methanol formation continued and the selectivity was 76–84 mol% (Figure 20.6). Throughout the test, the only products that were identified were methanol, CO, and water.

In the control tests of CO₂ reduction at 313K, $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ produced no products (Figure 20.7a1) whereas $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ produced trace amounts of methanol and CO at the formation rates of 0.023 and 0.0086 µmol h⁻¹ g_{cat}⁻¹ (Figure 20.7b1). Then, the methanol and CO formation (0.25 µmol h⁻¹ g_{cat}⁻¹ in total) using $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+(CO_3)^{2-} \cdot mH_2O$ under UV-visible irradiation (Figure 20.7a2) were proved to proceed via a band-gap excitation mechanism (Scheme 20.2). The methanol and CO formation rates using $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]_2^+[Cu(OH)_4]^{2-} \cdot mH_2O$ without light were only 4.7% and 12%, respectively, but not zero compared to those under UV-visible light.

20.6 CONCLUSIONS

The photoreduction of CO_2 using semiconductors is one of the new methods to reduce the CO_2 concentration in the atmosphere. If the photoreduction proceeds to form fuels (methanol, formic acid, or methane) by sunlight, this option will solve the problem of sustainable energy shortage simultaneously. The photoreduction of CO_2 in water was reported typically using TiO₂ at rates less than 1 µmol h⁻¹ g⁻¹_{cat}. The rates were improved to 1 – 10 µmol h⁻¹ g⁻¹_{cat} by dispersing Ti sites on microporous/mesoporous molecular sieves, by the addition of promoters, and under supercritical reaction conditions.

When we assume photocatalytic water splitting to form hydrogen, this is an alternative option to photoreduce CO₂ with hydrogen. Using TiO₂, ZrO₂, MgO, and Ga₂O₃, the photoreduction rates to CO were ~ 1 µmol h⁻¹ g_{cat}⁻¹. As a new category of semiconductor photocatalysts, layered double hydroxides (LDHs) consisting of Zn, Cu, Ga, or Al photoreduced CO₂ with H₂ to methanol at rates of 0.05–0.5 µmol h⁻¹ g_{cat}⁻¹ and to CO at rates of 0.07–0.18 µmol h⁻¹ g_{cat}⁻¹. The rates are not sufficient and less than the photoreduction of CO₂ in water using TiO₂-based photocatalysts, but the combination of divalent and trivalent elements for semiconductor LDHs will improve the efficiency. The major product methanol can be directly used as fuel, and the blank reaction test (no product) of CO₂ in H₂ at 313K in the dark using [Zn_{1.5}Cu_{1.5}Ga(OH)₈]₂⁺ (CO₃)^{2–} · mH₂O demonstrated actual photocatalytic formation of methanol and CO based on band-gap excitation mechanism [1,33].

Acknowledgments

The authors are thankful for financial support from a Grant-in-Aid for Scientific Research C (2255 0117, YI) from MEXT (2010–2012, YI), from the Iwatani Naoji Foundation (2011–2012, YI), from Asahi Glass Foundation (2009–2010, YI), and from the Promotion Section of Technology Innovation, Daikin Industries (2008–2009, YI). NA thanks Visiting Graduate Students Scholarship from Japanese Government (2008–2012).

References

- [1] N. Ahmed, Y. Shibata, T. Taniguchi, Y. Izumi, J. Catal. 279 (2011) 123–135.
- [2] J. Tollefson, Nature 473 (2011) 134–135.
- [3] A.J. Morris, G.J. Meyer, E. Fujita, Acc. Chem. Resear. 42 (2009) 1983–1994.
- [4] V.P. Indrakanti, J.D. Kubicki, H.H. Schobert, Energy Environ. Sci. 2 (2009) 745–758; Y. Izumi, Coor. Chem. Rev. 257 (2013) 171–186.
- [5] N.S. Lewis, D.G. Nocera, Proc. Natl. Acad. Sci. USA 103 (2006) 15729–15735.
- [6] R.D. Richardson, E.J. Holland, B.K. Carpenter, Nat. Chem. 3 (2011) 301–303.
- [7] A.M. Khenkin, I. Efremenko, L. Weiner, J.M.L. Martin, R. Neumann, Chem. Eur. J. 16 (2010) 1356–1364.
- [8] S.C. Roy, O.K. Varghese, M. Paulose, C.A. Grimes, Nano 4 (2010) 1259–1278.
- [9] I.A. Shkrob, T.W. Marin, H. He, P. Zapol, in: J. Phys. Chem. C 116 (2012) 9450–9460.
- [10] C.C. Lo, C.H. Hung, C.S. Yuan, J.F. Wu, Sol. Energy Mater. Sol. Cells 91 (2007) 1765–1774.
- [11] T. Yui, A. Kan, C. Saitoh, K. Koike, T. Ibusuki, O. Ishitani, Appl. Mater. Interfaces 3 (2011) 2594–2600.
- [12] S. Kaneco, H. Kurimoto, K. Ohta, T. Mizuno, A. Saji, J. Photochem. Photobiol. A 109 (1997) 59-63.
- [13] S. Kanoco, H. Kurimoto, Y. Shimizu, K. Ohta, T. Mizuno, Energy 24 (1999) 21–30.
- [14] T. Inoue, A. Fujishima, S. Konishi, K. Honda, Nature 277 (1979) 637-638.
- [15] C.C. Yang, Y.H. Yu, B. van der Linden, J.C.S. Wu, G. Mul, J. Am. Chem. Soc. 132 (2010) 8398–8406.
- [16] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, M. Honda, J. Phys. Chem. B 101 (1997) 2632–2636.
- [17] M. Anpo, H. Yamashita, K. Ikeue, Y. Fujii, S.G. Zhang, Y. Ichihashi, et al., Catal. Today 44 (1998) 327–332.

20. PHOTOCATALYTIC CONVERSION OF CARBON DIOXIDE INTO FUELS

- [18] J.S. Hwang, J.S. Chang, S.E. Park, K. Ikeue, M. Anpo, Topics Catal. 35 (2005) 311–319.
- [19] K. Kočí, L. Obalová, L. Matějová, D. Plachá, Z. Lacný, J. Jirkovský, O. Šolcová, Appl. Catal. B 89 (2009) 494–502.
- [20] K. Kočí, K. Matějů, L. Obalová, S. Krejčíková, Z. Lacný, D. Plachá, L.Čapek, A. Hospodková, O. Šolcová, Appl. Catal. B 96 (2010) 239–244.
- [21] S.S. Tan, L. Zou, E. Hu, Catal. Today 115 (2006) 269–273.
- [22] K. Ikeue, H. Yamashita, M. Anpo, T. Takewaki, J. Phys. Chem. B 105 (2001) 8350–8355.
- [23] K. Ikeue, S. Nozaki, M. Ogawa, M. Anpo, Catal. Today 74 (2002) 241-248.
- [24] C. Wang, R.L. Thompson, J. Baltrus, C. Matranga, J. Phys. Chem. Lett. 1 (2010) 48–53.
- [25] Y. Kohno, H. Hayashi, S. Takenaka, T. Tanaka, T. Funabiki, S. Yoshida, J. Photochem. Photobiol. A 12 (1999) 117–123.
- [26] Y. Kohno, T. Tanaka, T. Funabiki, S. Yoshida, Chem. Commun. (1997) 841–842.
- [27] K. Teramura, T. Tanaka, H. Ishikawa, Y. Kohno, T. Funabiki, J. Phys. Chem. B 108 (2004) 346–354.
- [28] K. Teramura, H. Tsuneoka, T. Shishido, T. Tanaka, Chem. Phys. Lett. 467 (2008) 191–194.
- [29] C.C. Yang, J. Vernimmen, V. Meynen, P. Cool, G. Mul, J. Catal. 284 (2011) 1-8.
- [30] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today 11 (1991) 173-301.
- [31] Y. Izumi, F. Kiyotaki, T. Minato, Y. Seida, Anal. Chem. 74 (2002) 3819–3823.
- [32] Y. Izumi, F. Kiyotaki, Y. Seida, J. Phys. Chem. B 106 (2002) 1518–1520.
- [33] N. Ahmed, M. Morikawa, Y. Izumi, Catal. Today, 185 (2012) 263–269.
- [34] Y. Sun, Y. Zhou, Z. Wang, X. Ye, Appl. Surf. Sci. 255 (2009) 6372–6377.
- [35] A. Ennadi, A. Legrouri, A. De Roy, J.P. Besse, J. Solid State Chem. 152 (2000) 568–572.
- [36] G.W. Brindley, S. Kikkawa, Clay. Clay. Miner. 28 (1980) 87-91.
- [37] D. Yan, J. Lu, J. Ma, M. Wei, S. Qin, L. Chen, D.G. Evans, X. Duan, J. Meter. Chem. 20 (2010) 5016–5024.
- [38] G. Leofanti, M. Padovan, M. Garilli, D. Carmello, A. Zecchina, G. Spoto, S. Bordiga, G. Turnes Palomino, C. Lamberti, J. Catal. 189 (2000) 91–104.
- [39] M. Morikawa, N. Ahmed, Y.Yoshida, Y. Izumi, submitted to J. Catal. on April 16, 2013.
- [40] I.H. Tseng, J.C.S. Wu, H.Y. Chou, J. Catal. 221 (2004) 432–440.
- [41] Y. Izumi, T. Itoi, S. Peng, K. Oka, Y. Shibata, J. Phys. Chem. C 113 (2009) 6706–6718.
- [42] Y. Izumi, K. Konishi, H. Yoshitake, Bull. Chem. Soc. Jpn. 81 (2008) 1241–1249.
- [43] Y. Izumi, Y. Shibata, Chem. Lett. 38 (2009) 912–913.
- [44] Y. Izumi, K. Konishi, D. Obaid, T. Miyajima, H. Yoshitake, Anal. Chem. 79 (2007) 6933–6940.
- [45] D. Masih, H. Yoshitake, Y. Izumi, Appl. Catal. A 325 (2007) 276–282.