the society for solid-state and electrochemical science and technology

Journal of The Electrochemical Society

Photoelectrochemical Carbon Dioxide Reduction to Hydrocarbons at Ambient Temperature and Pressure

Ronald L. Cook, Robert C. MacDuff and Anthony F. Sammells

J. Electrochem. Soc. 1988, Volume 135, Issue 12, Pages 3069-3070.
doi: 10.1149/1.2095490

Photoelectrochemical Carbon Dioxide Reduction to Hydrocarbons at Ambient Temperature and Pressure

Ronald L. Cook,* Robert C. MacDuff, and Anthony F. Sammells*

Eltron Research, Incorporated, Aurora, Illinois 60504

The identification of photoinduced CO_2 reduction pathways leading to gaseous hydrocarbon species would be an attractive strategy for producing gaseous fuels from this inorganic substrate molecule. Previous work toward this goal has pursued several paths including homogeneous catalysis (1), dispersed semiconductor suspensions (2-7), single crystal and polycrystalline photoelectrodes (8-10) and photoactivated gas-phase methanation catalysis (11). Of the dispersed semiconductor suspensions, n-$SrTiO_3$ has appeared to be the most active photocatalyst with adsorbed energy conversion efficiencies of ≅6% (4) being reported. Furthermore, both CO_2 (4) and HCHO (12) have been shown photoreduced to CH_4 in the presence of illuminated n-$SrTiO_3$ suspensions. On dispersed illuminated SiC both CO and CO_2 have been shown reducible to hydrocarbon products (6, 13). Reduction of CO_2 on illuminated SiC particles leads to HCOOH, HCHO, CH_3OH, and EtOH formation (13) whereas CO reduction has been shown to give CH_4, C_2H_4, C_3H_6, and C_3H_8[6] as reaction products with no alcohols being observed. Higher efficiencies for the above reduction reactions were observed after metal surface modification of SiC powder (*e.g.*, SiC/Pb, SiC/Rh, SiC/Fe) (13).

In recent years copper has been shown to be the most active electrocatalyst (14-18) for the electrochemical reduction of CO_2 or CO in aqueous $KHCO_3$. Major reduction products were found to be CH_4 and C_2H_4 with minor products being HCOOH and HCHO (14). Furthermore, we have recently found that formaldehyde can be reduced in aqueous electrolyte to give methane (19). For *in situ* electrochemically deposited copper electrodes, cumulative CO_2 reduction to CH_4 and C_2H_4, at current densities of 8 mA/cm^2 was found to be nearly faradaic (16). Reported here is the photoelectrochemical (PEC) reduction of CO_2 to CH_4, C_2H_4, and C_2H_6 using illuminated suspensions of p-SiC and Cu particles to CO_2-saturated potassium bicarbonate.

Experimental

Powdered −325 mesh semiconducting materials used in this work (n-WO_3, n-TiO_2, n-$BaTiO_3$, n-$SrTiO_3$, and p-SiC) were obtained from Cerac, Incorporated. p-SiC powder, emphasized here, was pretreated prior to use by boiling in 6*M* KOH to remove surface impurities such as SiO_2, Si, or C, followed by a thorough rinse with distilled water. PEC experiments were carried out in a Corning Glass 7740 reaction vessel (UV cutoff 275 nm, total volume 35 ml) containing 100 mg of the semiconductor powder in 10 ml aqueous 0.5*M* potassium bicarbonate and either $CuSO_4$ ($5 \times 10^{-4}M$) or copper powder (−100 mesh Alfa). CO_2 was initially passed through both hydrocarbon (Chemical Research Services, Incorporated) and oxygen (Oxy-Trap, Alltech Associates) traps prior to sparging into the continuously stirred semiconductor suspension in 0.5*M* $KHCO_3$. CO_2 was continually sparged through the solution at 20 ml min^{-1} during the experiment. Illumination of the reaction vessel was performed using an UltraViolet Products B-100A mercury UV lamp which gave an illumination flux of 7 mW/cm^2 at 365 nm on the reaction vessel surface (as measured by a Model 8-48 Eppley radiometer). Gaseous reaction products were sampled by use of a gas-tight syringe and septum port in the exit gas stream. Hydrocarbon products were analyzed using a GOW-MAC 69-750 gas chromatograph with an FID detector. A 6 ft stainless steel column with 80/100 mesh carbosphere packing (Alltech Associates) was used to separate hydrocarbon products. Specific surface area of the SiC powder following NaOH treatment was measured with a Micromeretic krypton surface analyzer using the Kr BET method. The specific surface area was found to be 0.24 m^2/g for the treated SiC powder. The specific surface area of the copper powder was found to be 0.02 m^2/g.

Results and Discussion

Initial experiments were performed using $CuSO_4$ ($5 \times 10^{-4}M$) and dispersed semiconducting powders (100 mg) in aqueous potassium bicarbonate electrolyte (*p*H 9). Previous work by others (20) has shown that copper could be deposited as the dark reaction onto illuminated semiconducting suspensions of n-TiO_2 and n-WO_3. No detectable gaseous hydrocarbon products were observed from illuminated dispersions of these n-doped metal oxides in CO_2 saturated 0.5*M* $KHCO_3$ either with or without trace $CuSO_4$ being present. Illuminated p-SiC suspensions in CO_2 saturated $KHCO_3$ solutions gave no hydrocarbon reaction products at *p*H 9. However, upon introducing $CuSO_4$ an initial CH_4 generation rate of 0.5 $\mu l\ h^{-1}\ g^{-1}$ was observed, which in terms of the p-SiC surface area (0.24 m^2/g) corresponded to a rate of 2.08 $\mu l\ m^{-2}\ h^{-1}$. Methane formation decayed to undetectable levels over ≅2h. Oxygen evolution was also observed as a PEC reaction product, although at 2-3 times lower levels than for hydrocarbons. Previous work suggests that the lower oxygen levels may, in part, be due to simultaneous photocorrosion of p-SiC. In particular, ESCA studies (21) have shown that SiC surfaces can become covered by a thin layer of SiO_2. For experimental work investigated here performance degradation with time may be attributed to surface oxide growth, copper deposition at photoactive sites on the p-SiC, or a combination of both these effects.

As a strategy to avoid or minimize copper codeposition onto photoactive p-SiC sites, which we suspect is, in part, responsible for progressively deteriorating CH_4 yields with time when $CuSO_4$ was present in the electrolyte, equimolar dispersed mixtures of p-SiC (100 mg) and Cu powder (160 mg) were introduced into CO_2 saturated $KHCO_3$ electrolyte. No gaseous hydrocarbons were observed from p-SiC/Cu mixtures in the dark or when illuminating either p-SiC or Cu separately in the electrolyte. However, upon illuminating dispersed p-SiC/Cu mixtures in the electrolyte, CH_4 was continuously observed as a reaction product. This strongly suggested that CO_2 reduction to CH_4 occurred at

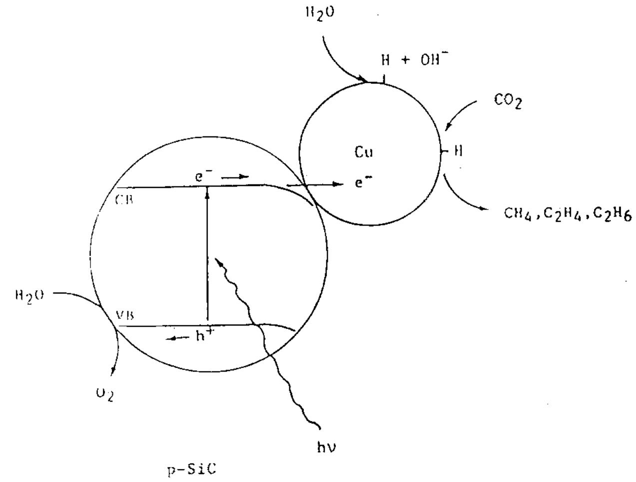

Fig. 1. Schematic of energetic processes occurring in the p-SiC/Cu system leading to formation of hydrocarbons from CO_2.

---

*Electrochemical Society Active Member.

Table I. Rates of photoelectrochemical hydrocarbon formation from CO_2 in the presence of p-SiC/Cu as a function of pH

	Hydrocarbon formation rates $\mu l\ h^{-1}\ g^{-1}$ ($\mu l\ m^{-2}\ h^{-1}$)		
pH	CH_4	C_2H_4	C_2H_6
3	4.0 (16.6)	—	—
5	14.9 (62)	3.9 (16.25)	2.3 (9.5)
6	8.5 (35.4)	t	t
7	7.1 (29.5)	t	t
9	2.2 (9.1)	—	—

t = trace.

copper particle sites after electron transfer from the p-SiC conduction band, as suggested schematically in Fig. 1. Previous workers have shown that when using Pd, surface modified SiC powders efficiencies for PEC CO_2 reduction to give condensed oxygenated species (*e.g.*, MeOH, HCOOH) increased upon going from neutral to acidic electrolyte. Furthermore, others (22) have reported that partial current for initial electron transfer during CO_2 reduction on Cu electrodes exhibit a maximum at ≅pH = 5.5. Thus it was of interest to evaluate hydrocarbon formation rates as a function of electrolyte pH. Table I summarizes hydrocarbon formation rates as a function of electrolyte pH for the CO_2 saturated $KHCO_3$ electrolyte at 40°C. Here, methane evolution increased as the electrolyte became more acidic, reaching a maximum rate of 14.9 $\mu l\ h^{-1}\ g^{-1}$ (62 $\mu l\ m^{-2}\ h^{-1}$) at pH 5. Further electrolyte acidification to pH 3 resulted in dramatic reduction in CH_4 evolution rates. At pH 5 ethylene and ethane were also observed as hydrocarbon products with formation rates of 3.9 $\mu l\ h^{-1}\ g^{-1}$ (16.25 $\mu l\ m^{-2}\ h^{-1}$) and 2.3 $\mu l\ h^{-1}\ g^{-1}$ (9.6 $\mu l\ m^{-2}\ h^{-1}$), respectively. At pH 5 these rates could be sustained over a period of 1-2h after which a slow decrease in hydrocarbon yields became evident. Similarities between observed maximum for pH dependent methane formation rates in illuminated p-SiC/Cu dispersions and partial current maxima for CO_2 reduction on copper electrodes (22) suggests that electron transfer to adsorbed CO_2 on copper sites may be rate determining. Lower yields at more acidic pH (~<5) may be due to either increased SiO_2 coverage on p-SiC sites (21) or competitive hydrogen formation.

The dependency of CO_2 reduction to methane using illuminated p-SiC/Cu dispersions was also examined over the temperature range 0°-80°C at pH 5. Between 30° and 60°C methanation was found relatively constant. However, at both higher (80°C) and lower (5°C) temperatures no hydrocarbon products could be observed by GC analysis. This observation is in contrast to previous work (14-18) on electrochemical CO_2 reduction at *in situ* deposited copper electrodes where CH_4 was found to be the dominant reaction product at 0°C and C_2H_4 at ambient temperatures. CO_2 reduction to give hydrocarbon products using illuminated semiconductor particles has been a relatively infrequent observation. p-SiC and n-SiC have previously been investigated for CO_2 reduction (6), although no gaseous hydrocarbon species were observed. When used as photocatalysts for the water gas shift reaction, the presence of C_1, C_2, and C_3 hydrocarbons were formed at low rates.

In experimental work discussed here, we have only analyzed for gaseous hydrocarbon products. We expect that C_1 oxygenated products such as CO, HCOOH, HCHO, and CH_3OH may also be present as previously found for CO_2 reduction on unmodified and metal surface modified SiC powders (13).

In conclusion, the formation of gaseous hydrocarbons at copper sites in aqueous $KHCO_3$ electrolytes can be driven photoelectrochemically using SiC/Cu powder dispersions.

Acknowledgments

The authors would like to thank Sherman S. Chao of the Institute of Gas Technology for performing krypton BET surface area measurements on p-SiC. Funding by the Gas Research Institute is gratefully acknowledged.

Manuscript submitted Jan. 29, 1988; revised manuscript received Aug. 9, 1988.

Eltron Research Incorporated assisted in meeting the publication costs of this article.

REFERENCES

1. B. Ulman, B. Aurian-Blajeni, and M. Halmann, *Isr. J. Chem.*, **22**, 177 (1982).
2. M. Halmann, M. Ulman, and B. Aurian-Blajeni, *Sol. Energy*, **31**, 429 (1983).
3. A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen, and A. Mackor, *Nouv. J. Chim.*, **6**, 373 (1982).
4. B. Aurian-Blajeni, M. Halmann, and J. Manassen, *Sol. Energy*, **25**, 165 (1980).
5. T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, **277**, 637 (1979).
6. D. H. M. W. Thewissen, A. H. A. Tinnemans, M. Eeuwhorst-Reinten, K. Timmer, and A. Mackor, *Nouv. J. Chim.*, **7**, 73 (1983).
7. Y. Taniguchi, H. Koneyama, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **55**, 2034 (1982).
8. S. Ikeda, M. Kosida, and K. Ito, *ibid.*, **58**, 1353 (1985).
9. M. Halmann, *Nature*, **277**, 115 (1978).
10. I. Taniguchi, B. Aurian-Blajeni, and J. O'M. Bockris, *Electrochim. Acta*, **29**, 923 (1984).
11. T. K. Ravindranathon, J. Kiwai, and M. Gratzel, *Nature*, **327**, 506 (1987).
12. A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen, and A. Mackor, in "Photochemical, Photoelectrochemical and Photobiological Processes," D. O. Hall and W. Palz, Editors, Reidel, Dordrecht (1982).
13. S. Kamamura, H. Kojima, J. Iyoda, and W. Kawai, *J. Electroanal. Chem.*, **225**, 287 (1987); **247**, 333 (1988).
14. Y. Hori, K. Kikuchi, and S. Suzuki, *Chem. Lett.*, 1695 (1985).
15. Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, *ibid.*, 897 (1985).
16. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *This Journal*, **134**, 1873 (1987).
17. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *ibid.*, **134**, 2375 (1987).
18. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *ibid.*, **135**, 1320 (1988).
19. R. L. Cook, R. C. MacDuff, and A. F. Sammells, Unpublished results.
20. H. Reiche, W. W. Dunn, and A. J. Bard, *J. Phys. Chem.*, **83**, 2248 (1979).
21. M. Morisaki, H. Ono, and K. Kazawa, *This Journal*, **131**, 2081 (1984).
22. A. V. Zakharyan, N. V. Osetrova, and Yn. B. Vasil'ev, *Elecktrokhimiya*, **13**, 1818 (1977).