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Reduction of CO_2 by H_2 and Water Vapor over Metal Oxides Assisted by Visible Light

1. INTRODUCTION

Activation of CO_2 using homogeneous transition metal catalysts is an area of considerable current interest. However, no intensive studies on the activation of CO_2 by heterogeneous catalysts have been reported except for studies on the role of CO_2 in methanol synthesis over oxide catalysts (*1*). Formates have been observed as intermediates in the interaction of CO_2 and H_2 over ZnO (*2*) and in the water-gas shift reaction over Cu/ZnO (*3*). The reduction of CO_2 by H_2O over illuminated finely divided semiconductors has been reported (*4–6*). We report here the results of an initial investigation of the photoassisted reduction of CO_2 by H_2 and H_2O vapor over metal oxides. There appear to be no prior reports on the subject of this paper. The work which is summarized here provides the basis for mechanistic suggestions.

1.1 Choice of Catalysts

Several oxide systems were chosen for investigation. α-Fe_2O_3, an *n*-semiconductor with a band gap of 2.0 eV, can absorb ~50% of the insolation flux at ground level and catalyzes the photoreduction of carbon dioxide by water (*4, 6*). Zn-Fe-oxide is a normal spinel having Fe^{3+} in octahedral sites and *n*-semiconductivity (*7*). It is ferromagnetic with a low Curie point of 333°K. Platinized La-Ni-oxide, a narrow-band electronic conductor with Ni^{3+} in octahedral sites of cubic perovskite, catalyzes photoreduction of CO_2 by water (*6*). Incorporation of Co, Ni, or Mn promotes the hydrodesulfurization activity of MoO_3 supported on γ-Al_2O_3 (*8*). Further, change in the support from insulating γ-Al_2O_3 to semiconducting *n*-TiO_2 ($E_g = 3.1$ eV) could improve light-absorption characteristics and activity of Co–Mo catalysts.

2. MATERIALS AND METHODS

2.1 Materials

α-Fe_2O_3 (Baker AR) was used without further treatment. Zn–Fe oxide was prepared by the decomposition of mixed hydroxides (*9*) of Zn and Fe (1 : 2 molar ratio) at 1273°K. *Platinized La-Ni-Oxide* was obtained by platinizing La-Ni-oxide which was prepared by decomposing an equimolar mixture of the oxalates of La and Ni (*10*) between 1073 and 1273°K in a current of dry oxygen. The oxide was treated with 0.1 wt% chloroplatinic acid, dried in argon at 573°K, reduced with flowing hydrogen for 3 h at the same temperature, and stabilized with air. *Co-Mo-Al-oxide* (4.5% CoO : 15% MoO_3 : 80.5% Al_2O_3) was produced by mixing dried γ-Al_2O_3 (Alfa), with alcoholic ammoniacal solutions of cobaltous nitrate and ammonium molybdate, evaporating to dryness, and heating at 873°K in flowing argon. The oxide was subsequently treated with H_2 at 473–573° K for ½ h and then stabilized with air. *Co-Mo-Ti-oxide* was prepared by a procedure similar to that used for Co-Mo-Al-oxide. γ-Al_2O_3 was replaced by *n*-TiO_2 (deGussa) and the composition by weight of the preparation was kept at 3.5% CoO : 10% MoO_3 : 86.5% TiO_2. Very high purity Linde N_2, Ar, and H_2 and Welders' Supply CO_2 were used without further purification. In a few cases, the CO_2 was purified by bubbling it through a solution of chromous perchlorate in perchloric acid and then through water. Water

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which had been both double-distilled and deionized was used in all cases.

2.2 *Methods*

(*a*) *Deposition of catalyst.* Finely ground oxide (100 mg) was made into a smooth paste with water and spread on one of the larger (5.0 × 5.0 cm) surfaces of the Pyrex illumination cell. The film was then dried in air at 473°K for 24 h.

(*b*) *Conditioning of catalyst films.* Immediately before use, oxide films on glass were purged with a current of pure dry N_2 for 4 h followed by H_2 for 30 min, both at 303°K in the dark. Whenever the conditions were changed in a series of reactions with a given film, the oxide film was purged with pure N_2 for 12 h at 303°K followed by treatment with H_2 at 303°K, both in the dark, immediately before reaction. The pretreatment with H_2 was omitted in experiments which are summarized in Sections 3.2 and 3.3 below.

(*c*) *Reaction.* Photoassisted reduction of CO_2 by H_2 and H_2O vapor was conducted in a thermostated Pyrex glass cell under illumination from a 150-W Xe lamp. The lamp was placed 30 cm from the cell and a 420-nm cut-off filter (Oriel 5128-5148) was placed between the cell and the lamp. The reaction temperature was maintained at 303 ± 0.1°K.

A reaction mixture consisting of 2–3 : 1 (v/v) $H_2 : CO_2$ saturated with H_2O vapor was passed over the catalyst under illumination at a rate of 50–60 ml/min at atmospheric pressure. The reaction was allowed to proceed for 2 h before commencing the collection of products. The liquid products were trapped by passing the effluent gas through 10–20 ml of ice-cooled water. Reaction times varied from 10 to 30 h.

(*d*) *Analysis.* The liquid products were analyzed by gas chromatography on a Porapak-Q column using FID. Formic acid was further identified by its uv absorption spectrum (*11*), measured on a Cary Model 118C spectrophotometer. Formaldehyde was determined by the chromotropic acid method (*12*). CO was detected by the NBS Pd-silicomolybdate method (*13*).

3. RESULTS AND DISCUSSION

3.1 *Survey of Reaction with Simultaneously Supplied H_2 and Water Vapor*

Data are summarized in Table 1. The results show a range of activities for the five

TABLE 1

Reaction of CO_2, H_2, and Water Vapor on Illuminated Oxide Films at 303°K

Catalyst	Sequence of experiments	Illuminated	Period of reaction (h)	Integral rates of products formation, μmole/h				
				HCO_2H	CH_2O	MeOH	MeCHO	MeCOMe
α-Fe_2O_3	1	No	20	Tr	0	Tr	0	0
α-Fe_2O_3	2	Yes	32	10.9	0.03	0.07	Tr	0
α-Fe_2O_3	3	Yes	29	6.9	Tr	0.03	0	0
α-Fe_2O_3	4	Yes	30	4.4	0.02	0.12	Tr	Tr
α-Fe_2O_3	5	Yes	24	4.0	0.03	0.14	0	Tr
Zn-Fe-Oxide	1	No	24	Tr	0	Tr	0	0
Zn-Fe-Oxide	2	Yes	3	37.7	Tr	0.37	0	0
Zn-Fe-Oxide	3	Yes	22	17.8	0.05	0.05	Tr	0
Zn-Fe-Oxide	4	Yes	22	9.0	Tr	0.11	0	0
Platinized La-Ni-Oxide	1	No	24	0	0	0	0	0
Platinized La-Ni-Oxide	2	Yes	24	38.9	0.05	0.08	0.06	0
Co-Mo-Al-Oxide	1	No	48	Tr	Tr	Tr	0	0
Co-Mo-Al-Oxide	2	Yes	9	16.0	0.11	0.19	0.07	0
Co-Mo-Ti-Oxide	1	No	50	Tr	0	Tr	0	0
Co-Mo-Ti-Oxide	2	Yes	24	13.2	0.07	0.09	0.19	0.05

TABLE 2

Evidence for the Roles of H_2 and H_2O Vapor in the Reduction of CO_2 over Illuminated Oxide Films at 303°K

Catalyst	Sequence of Expts.	Illuminated	H_2	H_2O	Integral rates of formation of products, μmole/h		
					HCO_2H	CH_2O	MeOH
	Part I: Role of H_2 in Presence of H_2O Vapor						
α-Fe_2O_3	1	Yes	No	Yes	0	Tr	0.02
α-Fe_2O_3	2	Yes	Yes	Yes	0.9	Tr	0.10
Zn-Fe-Oxide	1	Yes	No	Yes	Tr	0.02	0.02
Zn-Fe-Oxide	2	Yes	Yes	Yes	1.9	Tr	0.11
Platinized La-Ni-Oxide	1	Yes	No	Yes	Tr	0.09	0.02
Platinized La-Ni-Oxide	2	Yes	Yes	Yes	3.0	0.01	0.10
Platinized La-Ni-Oxide	3	Yes	Yes	Yes	6.8	0.01	0.15
Co-Mo-Al-Oxide	1	Yes	No	Yes	Tr	0.04	0.05
Co-Mo-Al-Oxide	2	Yes	Yes	Yes	2.6	0.01	0.20
	Part II: Role of H_2O Vapor in Presence of H_2						
α-Fe_2O_3	1	No	Yes	No	0	0	0
α-Fe_2O_3	2	Yes	Yes	No	0	0	0
α-Fe_2O_3	3	Yes	Yes	Yes	1.4	0.01	0.08
α-Fe_2O_3	4	Yes	Yes	No	0.5	0	0.02
Zn-Fe-Oxide	1	No	Yes	No	0	0	0
Zn-Fe-Oxide	2	Yes	Yes	No	0	0	0
Zn-Fe-Oxide	3	Yes	Yes	Yes	4.1	0.02	0.13
Zn-Fe-Oxide	4	Yes	Yes	No	1.0	0	0.02
Platinized La-Ni-Oxide	1	No	Yes	No	0	0	0
Platinized La-Ni-Oxide	2	Yes	Yes	No	0	0	0
Platinized La-Ni-Oxide	3	Yes	Yes	Yes	4.9	Tr	0.11
Platinized La-Ni-Oxide	4	Yes	Yes	No	1.1	0	Tr
Co-Mo-Al-Oxide	1	No	Yes	No	0	0	0
Co-Mo-Al-Oxide	2	Yes	Yes	No	0	0	0
Co-Mo-Al-Oxide	3	Yes	Yes	Yes	2.6	0.05	0.11
Co-Mo-Al-Oxide	4	Yes	Yes	No	0.8	0	Tr

catalysts studied. Formic acid was the major condensible product, accompanied by small yields of formaldehyde, acetaldehyde, and methanol with traces of ethanol and acetone. CO was also observed in the gas stream. Formation of condensible products over α-Fe_2O_3 or Zn-Fe-oxide was not detectable in the absence of light. The photoassisted activities for various systems are described below.

At 303°K, Pt-La-Ni-oxide displayed the highest activity and selectivity toward formic acid production, with an integral rate of formation of 39 μmole h^{-1}. This was followed by Co-Mo-Al-oxide, Co-Mo-Ti-oxide, and Fe_2O_3 which showed integral rates of formation of formic acid of, respectively, 16, 13, and 11 μmole h^{-1}. The rate of formic acid production over α-Fe_2O_3 decreased with time. The rate of formation of formic acid at 333°K over Zn-Fe-oxide decreased in 25 h to less than 50% of its initial value. The integral rate at 303°K observed after this period was similar to the integral rate observed with Fe_2O_3 in the first 32 h.

3.2 Effect of H_2 on Reaction of CO_2 with Water Vapor

Experiments testing the effect of added H_2 on the reaction of CO_2 and water vapor over films of several metal oxides are summarized in Table 2. These data were obtained with films which had been used in experiments discussed in Section 3.3, below. These films were first reconditioned for 12 h by purging with flowing N_2 at 303°K under illumination. With each of the catalysts, reaction of CO_2 and H_2O vapor in the absence of added H_2 gave low rates of production of formaldehyde and methanol with only traces of formic acid. In every case, addition of H_2 greatly increased the integral rate of production of formic acid so that it became the principal product. Upon addition of H_2, formaldehyde yields were diminished while integral rates of formation of methanol increased about fivefold in each case. In no case, however, did the rate of formation of formic acid approach the values reported in Table 1. A possible interpretation is that the half-hour preconditioning of catalysts with H_2 and/or subsequent passage of H_2, water vapor, and CO_2 over the illuminated catalyst for 2 h prior to collection of products, the procedures used before collecting the data of Table 1 but *not* used before collecting the data of Table 2, activated the catalysts. This interpretation is supported by one experiment with Pt-La-Ni-oxide, the results of which are recorded in Table 2. In this experiment, the film, which had already been used in the preceding experiment recorded in Table 2, was purged with flowing Ar for 12 h at 333°K and then treated with pulses of H_2 for 30 min at 303°K. The integral rate of formation of formic acid more than doubled although it was still less than 20% of that reported in Table 1 for this catalyst.

3.3 Effect of Water Vapor on Reaction of CO_2 with H_2

The role of water vapor in the reduction of CO_2 was tested using fresh films of oxide. Results are summarized in Table 2. In the absence of H_2O vapor, no condensable products were detected with any of the catalysts either in the dark or under illumination. Upon introduction of water vapor, formic acid was the principal condensable product produced by the photoassisted reaction over all the catalysts, together with minor amounts of formaldehyde and methanol. Subsequent elimination of water from the reactant stream resulted in sharp decreases in activity.

The integral rates of formation of formic acid obtained when CO_2, H_2, and water vapor were reacted as described in this section and Section 3.2 were similar and almost an order of magnitude less than those summarized in Table 1. It is notable that the same catalyst films were used to obtain the data of Sections 3.2 and 3.3.

3.4 Production of CO from H_2 + CO_2

Carbon monoxide was identified qualitatively as a product when mixtures of CO_2 and H_2 were passed over any of the catalysts employed either with or without H_2O vapor and both under illumination and in the dark. No CO was observed in the absence of catalyst.

3.5 Discussion

It can be concluded from the data presented above that H_2, H_2O, and catalyst all play essential roles in the observed reduction of CO_2 to formic acid and that absorption of light by the catalyst is also necessary. The data do not discriminate among alternative mechanistic models and it is only possible to speculate about possible options. Neither do the data reveal whether H_2 or H_2O or both is the source of reducing equivalents.

(*a*) *Role of photoactivation of the catalyst.* The Zn-Fe-oxide and α-Fe_2O_3 used in this work are *n*-type semiconductors which underwent photopromotion of electrons into their conduction bands, as did platinized La-Ni-oxide a narrow-band electronic conductor. However, in the absence of information on quantum yields for formation of formic acid and their dependence on the wavelength of absorbed light there is no basis for deciding on whether catalytic action involved materials acting as photodiodes (*14*). Alternative modes of activation by light, e.g., involving photodissociation of chemisorbed H_2 or water or photoexcitation of chemisorbed CO_2 must also be considered.

(*b*) *Formation of CO and its hydration.* The ubiquitous formation of CO from CO_2 and H_2 in the presence or absence of H_2O and light suggests a reaction pathway proceeding via the reverse water-gas shift reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (1)$$

Compounds of Fe, Co, and Mo are good catalysts for this reaction (*15, 16*). Since the presence of H_2O as well as H_2, is required for photoassisted reduction of CO_2 to formic acid, one possible reaction channel is the photoassisted hydration of CO

$$CO + H_2O \rightleftarrows HCO_2H \tag{2}$$

(*c*) *Reaction paths which do not involve CO.* The requirement that H_2O vapor be supplied suggests reaction channels involving hydration of catalysts to give relatively acidic M–O–H sites capable of capturing CO_2 to form bicarbonate

$$CO_2(g) + M\text{–}O\text{–}H(s) \rightarrow M\text{–}O\text{–}CO_2H(s) \tag{3}$$

Hydrogen adsorbed as dihydrogen or dissociatively at adjacent sites may reduce such metal bicarbonates to formate with ultimate hydrolysis to free formic acid. Either the dissociation of H_2, or the reduction of bicarbonate to formate, or both, might be photodriven. The sensitivity of rates of formation of formic acid to pretreatment procedures suggests the importance of appropriate juxtaposition of different adsorbed molecules.

Further work is required to sort out the mechanistic possibilities.

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REFERENCES

1. Klier, K., "Advances in Catalysis," Vol. 31, p. 243. Academic Press, New York, 1982.

2. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **66,** 756 (1970).

3. Davydov, A. A., Boreskou, G. K., Yuréva, T. M., and Rubene, N. A., *Dokl. Akad. Nauk USSR* **236,** 1402 (1977).

4. Aurian-Blajeni, B., Halmann, M., and Manassen, J., *Solar Energy* **25,** 165 (1980).

5. Inoue, T., Fujishima, A., Konishi, S., and Honda, K., *Nature* (*London*) **277,** 637 (1979).

6. Lichtin, N. N., and Vijayakumar, K. M., Extended Abstract of the 163rd Meeting of the Electrochemical Soc. No. 516, *J. Electrochem. Soc.* **130,** 108C (1983).

7. Galasso, F., "Structure and Properties of Inorganic Solids," p. 217. Pergamon, New York, 1970.

8. Massoth, F. E., "Advances in Catalysis," Vol. 27, p. 266. Academic Press, New York, 1978.

9. Chalyi, V. P., Lukachina, E. N., and Potomkin, K. W., *Isv. Akad. Nauk SSSR Inorg. Mater.* **5,** 2136 (1969).

10. Goodenough, J. B., and Raccah, P. M., *J. Appl. Phys.* **36,** 1031 (1965).

11. Adams, G. E., and Hart, E. J., *J. Amer. Chem. Soc.* **84,** 3996 (1962).

12. Lichtin, N. N., *J. Phys. Chem.* **63,** 1449 (1959).

13. Sheperd, M., *Anal. Chem.* **19,** 77 (1947).

14. Nozik, A. J., *Ann. Rev. Phys. Chem.* **29,** 189 (1978).

15. Newsome, D. S., *Catal. Rev.-Sci. Eng.* **21,** 275 (1980).

16. Krylov, O. V., "Catalysis by Nonmetals," p. 151. Academic Press, New York, 1970.

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