JOURNAL OF CATALYSIS **104**, 246–251 (1987)

Photoassisted Reduction of CO_2 by H_2 over Metal Oxides in the Absence and Presence of Water Vapor

1. INTRODUCTION

We have previously reported initial results of an investigation of the photoassisted reduction of CO_2 by H_2 over α-Fe_2O_3, Zn-Fe-oxide, platinized La-Ni-oxide, Co-Mo-Al-oxide and Co-Mo-Ti-oxide in the absence and presence of water (*1*). We now report more extensive quantitative yield data for the same reactant systems with the same catalysts, as well as with platinized $SrTiO_3$, and the relationship of yields to incident and absorbed light energy. The data are compared with calculated gas phase equilibrium compositions and it is shown that, with the most active catalyst, Co-Mo-Al-oxide, photoassisted consumption of CO_2 in the presence of water vapor under arbitrarily chosen conditions was about 10 times greater than would be expected from gas phase equilibration. Over this catalyst, the observed efficiency of use of incident photons was 0.35 molecules of photoproduct per incident photon, corresponding to an estimated quantum yield of 1 molecule of photoproduct per photon absorbed by the catalyst.

2. MATERIALS AND METHODS

2.1. Catalysts and reactants. Preparations of the previously reported catalysts and the sources and grades of the reagents used in these preparations and of H_2, Ar, and CO_2 were as described previously (*1*). High-purity He was supplied by Linde. Pfaltz and Bauer research grade $SrTiO_3$ was platinized (*1*) by treatment with 0.1 wt% aqueous chloroplatinic acid and dried in Ar at 200°C. As previously reported, the atomic ratio of Zn to Fe in Zn-Fe-oxide was 1 : 2 and that of La to Ni in La-Ni-oxide was 1 : 1. The composition of Co-Mo-Al-oxide was 4.5 wt% CoO, 15 wt% MoO_3, and 80.5 wt% Al_2O_3 while that of Co-Mo-Ti-oxide was 3.5 wt% CoO, 10 wt% MoO_3, and 86.5 wt% TiO_2.

2.2. Catalyst films. Procedures for preparation of films were essentially as previously reported (*1*) except that He was used in place of N_2 for preconditioning films.

2.3. Reaction apparatus. Reactions were performed in 5 × 5 × 1-cm or 4 × 7 × 2-cm flowthrough cells with flat major faces. A cell was connected to gas flow system which provided reactants and carried the gas stream beyond the cell to a sampling valve coupled to the analytical system. The reaction cell was immersed in a water bath thermostatted to ±0.05°C. Illumination was by a 200-W Schoeffel Hg-Xe lamp equipped with a collimating lens system and mounted on an optical bench at a distance of 45 cm from the cell. Short-wavelength ultraviolet and long-wavelength infrared were eliminated by respectively a 350-nm Corning cut-off filter and the water bath. The light beam was split and the relative intensity of the light flux incident on the cell was continuously monitored with a Model 4382 Pacific Instruments photomultiplier connected to a recorder.

2.4. Reaction conditions and analyses of products. Reactions at the gas–solid interface were carried out at 1 atm and 29.8°C by passing 59–64 ml/min of a mixture of H_2 and CO_2 at a molar ratio of respectively 1.85–2.13 to 1 for 3 to 22 hr. Condensable products were trapped in 10–20 ml of water

0021-9517/87 $3.00

maintained at 0°C. Water vapor, when present, was at a molar ratio of 0.03 to 1 relative to CO_2. Collection of condensible products and sampling of the reacted gas stream were started 30 min after reaction was begun. Products were analyzed with a Perkin–Elmer Sigma 300 gas chromatograph equipped with gas-sampling and column-switching valves, thermal conductivity and flame ionization detectors in series, and a Perkin–Elmer LCI-100 computing integrator. Products trapped in water were analyzed on a Porapak-N column while products sampled from the gas stream downstream from the ice-trap were analyzed on Porapak-N and MS-5A columns, used in series with column switching. Formation of formic acid was confirmed spectrophotometrically (*2*) using a Cary 210 instrument. Formaldehyde was determined by the chromotropic acid method (*3*). Production of CO was qualitatively confirmed by the NBS Pd-silicomolybdate method (*4*).

2.5. *Actinometry.* The incident light flux was measured by ferrioxalate actinometry (*5*) and the resulting data were used to calibrate the on-line photometer. Potassium oxalate monohydrate was Baker analyzed reagent, ferric chloride hexahydrate and sodium acetate trihydrate were both Fisher ACS reagent grade, and phenanthroline monohydrate was Smith ACS reagent grade. A 350- to 480-nm bandpass filter was used in optical series with a 350-nm cut-off filter to isolate the lamp flux at 350–480 nm. The only significant components of the Hg-Xe lamp emission at 350–480 nm are the mercury bands at 366, 405, and 436 nm. In addition, the filters passed some light at wavelengths above 700 nm. The total flux from the lamp which was incident on the cell was calculated from the actinometric data, the known characteristics of the filters, and the known emission spectrum of the lamp. Four replicate measurements gave a value for the total lamp flux from 350 to 1000 nm of $(1.02 \pm 0.08) \times 10^{17}$ quanta/sec. The uncertainties in calculating the total flux from the actinometric data are probably greater than the quoted standard deviation, which was calculated from the experimental reproducibility. Based on the above value of the flux and the illuminated area of the cell, 7.1 cm^2, the spatially averaged flux was 1.4×10^{16} quanta/sec-cm^2. Fluctuations calculated from variations in photometer readings were negligible.

3. RESULTS

3.1. *Products from Reaction of CO_2 with H_2 in the Absence of Water Vapor*

No products were detectable from reaction in the dark or under illumination in the absence of any catalyst. Yields of products formed in the presence of catalysts are summarized in Table 1. CO was the major product formed over all the catalysts and CH_4 was the principal minor product. Formic acid was not detectable in the absence of water vapor. All the catalysts which were investigated promoted reduction in the dark. Yields increased by a factor of 2–4.5 upon illumination of catalyst films, demonstrating that photoassisted reaction occurs with all the catalysts. Yields of CO were measured after both 3 and 20–22 hr of illumination. With all the catalysts, the average rate of production of CO, i.e., the total yield divided by the period of illumination, was independent of the period of illumination, indicating that catalytic activity remained constant for at least 20–22 hr.

3.2. *Products from Reaction of CO_2 and H_2 in the Presence of Water Vapor*

No product was detectable in the dark or under illumination in the absence of any catalyst. Results obtained in the presence of water vapor, summarized in Table 1, were independent of whether the reaction time was 3 or 20–22 hr. The presence of water vapor had little effect on dark yields of CO except over Co-Mo-Ti-oxide, where

TABLE 1

Average Rates of Production of Products in the Reaction of Flowing[a] CO_2 and H_2 over Films of Metal Oxides[b] at 1 atm[c] and 29.8°C

Catalyst	Photo-assisted	Average rate of production in the absence of H_2O(g) (μmole/hr)		Average rate of production in the presence of H_2O(g) (μmole/hr)				
		CO	CH_4	CO	CH_4	HCO_2H	CH_2O	CH_3OH
α-Fe_2O_3	No	58	—	54	—	—	—	—
	Yes	116	—	102	0.11	8.9	Tr	0.10
Zn-Fe-oxide	No	110	—	114	Tr	—	—	—
	Yes	234	0.29	215	0.36	20.1	Tr	0.11
Co-Mo-Al-oxide	No	64	—	59	Tr	—	—	—
	Yes	280	0.41	267	0.41	19.3	Tr	0.21
Co-Mo-Ti-oxide	No	88	—	102	—	—	—	—
	Yes	138	0.12	126	Tr	14.8	Tr	0.07
Pt-La-Ni-oxide	No	102	—	108	—	—	—	—
	Yes	158	0.21	160	0.22	30.8	Tr	0.15
Pt-$SrTiO_3$	No	64	—	59	—	—	—	—
	Yes	172	0.32	160	0.31	10.6	Tr	0.06

[a] 16–17 mmol/hr.

[b] 0.15–0.20 g of finely ground catalyst in 25 or 28-cm^2 films.

[c] Partial pressures: CO_2, 0.33 ± .02 atm; H_2, 0.68 ± .04 atm; H_2O when present, 0.01 atm.

a 14% decrease was observed. Methane, in trace amounts, was the only product other than CO which was detected in the dark reaction. Under illumination, yields of formic acid corresponding to 6.6–19 mole% of the yields of CO were obtained. With all the catalysts except one, the sum of the yields of formic acid and CO obtained under illumination differed by only 0.04–4.5 mole% from the yield of CO obtained under illumination in the absence of water vapor. With platinized La-Ni-oxide, the sum of the yields of these two products corresponded to 21 mole% more than the yield of CO in the absence of water vapor. Minor products which were also observed in the photoassisted reaction in the presence of water vapor included CH_4 corresponding to 0.2 mole% or less of the yields of CO, CH_3OH corresponding to 0.01 mole% or less of the yields of CO, and traces of formaldehyde.

3.3. Efficiencies of Chemical Use of Incident and Absorbed Photons

The determination of the magnitude of the incident light flux is described in Section 2.5, above. It is assumed here that the absolute error in the flux is no larger than 0.3×10^{17} quanta/sec. The estimated error in yields of products and their average rate of production is ±5%, or less. Thus, it is assumed that efficiencies of use of *incident* photons given in this paper have a reliability of about ±35%. Values of efficiencies of use of incident photons, E_i = (molec. of photoproduct/sec)/(quanta incident/sec), calculated from the data of Table 1, are given in Table 2. Rates of formation of photoproducts were obtained by subtracting rates of the dark reaction from corresponding rates under illumination.

For each of the six catalysts, values of E_i

TABLE 2

Efficiencies[a] of Utilization of H_2 and Photons in the Reaction of CO_2 with H_2 over Metal Oxides in the Absence and Presence of Water Vapor[b]

Catalyst	Water vapor	Photo-assisted	Efficiencies of use		
			H_2 (%)	Photons	
				E_i	E_q
α-Fe_2O_3	No	No	0.06	—	—
	No	Yes	0.11	0.10	0.15
	Yes	No	0.05	—	—
	Yes	Yes	0.10	0.09	0.14
Zn-Fe-oxide	No	No	0.11	—	—
	No	Yes	0.24	0.20	—
	Yes	No	0.11	—	—
	Yes	Yes	0.24	0.20	—
Co-Mo-Al-oxide	No	No	0.07	—	—
	No	Yes	0.28	0.34	0.98
	Yes	No	0.07	—	—
	Yes	Yes	0.29	0.37	1.03
Co-Mo-Ti-oxide	No	No	0.09	—	—
	No	Yes	0.14	0.08	0.23
	Yes	No	0.10	—	—
	Yes	Yes	0.14	0.06	0.18
Platinized La-Ni-oxide	No	No	0.10	—	—
	No	Yes	0.16	0.09	0.09
	Yes	No	0.11	—	—
	Yes	Yes	0.19	0.14	0.14
Platinized $SrTiO_3$	No	No	0.07	—	—
	No	Yes	0.17	0.18	0.71
	Yes	No	0.06	—	—
	Yes	Yes	0.17	0.18	0.73

[a] Efficiencies in the presence of water vapor are based on sums of the yields of CO and HCO_2H. Values of E_i and E_q are expressed in pure numbers, *not* in percent.

[b] Conditions given in Table 1.

in the presence and absence of water vapor are similar. Over the entire range of the experiments, E_i varies from 0.06 (with Co-Mo-Ti-oxide in the presence of water vapor) to 0.37 (with Co-Mo-Al-oxide in the presence of water vapor). Although the absolute values of E_i are estimated to be uncertain to around ±35%, only the uncertainty in product yields, i.e., ±5%, is pertinent to their relative values.

An additional source of uncertainty enters into the estimate of quantum efficiencies, E_q = (molec. of photoproduct/sec)/(quanta absorbed/sec). Rather than measuring the rate of absorption of photons by the catalysts, it has been assumed that all incident photons with energies equal to or greater than the band-gap of a given semiconductor were absorbed. The corresponding values of absorbed photon flux were then calculated from the measured incident flux with the aid of the emission spectrum of the Hg-Xe lamp. Literature values (*6*) of the band gaps of α-Fe_2O_3 and $SrTiO_3$ were estimated to correspond to absorption of respectively 64% (2.2 eV) and 25% (3.2 eV) of the incident photon flux. The literature value (*6*) of the band-gap of MoO_3 (2.9 eV) was used to estimate the fraction of incident light absorbed by the two cobalt-containing oxides as 36%. La-Ni-oxide, a narrowband electronic conductor (*7*), is assumed to absorb the entire incident photon flux. No data on the band-gap of Zn-Fe-oxide appears to be available. Values of E_q are presented in Table 3. It is noteworthy that the highest values of E_q, obtained with Co-Mo-Al-oxide in the presence and absence of water vapor, are indistinguishable from unity.

4. DISCUSSION

4.1. Evidence of Catalytic Action

The probability of the metal oxides used in this research functioning as significant sources of reducing equivalents is small. With two exceptions, metallic Pt and Co(II), all the metals were present in their highest common oxidation states, namely, Fe(III), Zn(II), Mo(VI), Al(III), Ti(IV), La(III), Ni(III), and Sr(II). The possibility that either Pt, Co(II), or impurities were

TABLE 3

Comparison of Observed Conversion of CO_2 over Co-Mo-Al-Oxide at 30°C and 1 Min Residence Time with Gas Phase Equilibrium Conversion[a]

Concentrations of Reactants (m*M*)			% Conversion		
CO_2	H_2	H_2O	Calculated equilibrium	Dark	Observed photoassisted
11.9	28.1	—	0.54	0.15	0.65
13.2	27.0	0.54	0.06	0.12	0.60[b]

[a] Conditions given in Table 1.

[b] Based on sum of yields of CO and HC_2OH.

significant reactants can be evaluated from the number of reducing equivalents required to produce the observed yields. For example, 5.9 mmole of CO and formic acid were produced in 22 hr of photoassisted reaction over Co-Mo-Al-oxide in the presence of water vapor, corresponding to 11.8 millireducing equivalents. Assuming 200 mg of catalyst (see Section 2.2), the 4.5 wt% of CoO present in it corresponded to only 0.12 millireducing equivalents. Similarly, the 4.6 meq of reduced products obtained in 21 hr of photoassisted reaction over α-Fe_2O_3 in the presence of water vapor can be compared with the 1.25 mmole of the catalyst present in 200 mg of this compound. Similar consideration of the data for all the catalysts demonstrates that in no case could a substantial part of the observed products have resulted from reaction with catalyst or impurity.

4.2. Consumption of H_2

Data on consumption of H_2, which is summarized in Table 3, are based on yields of CO and HCO_2H, measured flow-rates of H_2, and the assumption that only CO and H_2O or HCO_2H were produced in the reaction. Utilization of H_2 appears to be inefficient. However, no effort was made to optimize it by, e.g., recirculating it in a closed system.

4.3. Implication of Estimated Quantum Yields

The highest values of E_q recorded in Table 3 are 1.0 for Co-Mo-Al-oxide and 0.7 for TiO_2. If it is assumed that both these values reflect conversion efficiencies which differ little from unity, they can provide some insight into the photoassisted process. The units of E_q are molecules of product produced per absorbed photon. However, CO_2 is actually reduced by 2 reducing equivalents. An electron-transfer mechanism in which one photon promotes transfer of two electrons is not plausible. More probable are mechanisms in which absorption of a photon by the catalyst results in activation of a sorbed molecule so that it then undergoes reaction. Photoactivation of sorbed CO_2 in this fashion is an example of such a process. A practical implication of the observed values of E_q is the possibility that, if quantum yields are independent of light intensity at substantially higher intensities, proportionally higher rates of reaction can be obtained.

4.4. Relationship between Photoassisted Yields in the Presence and Absence of Water

The fact that photoassisted yields of CO in the absence of water differ little from the sum of photoassisted yields of CO plus HCO_2H in the presence of water supports the conclusion that the principal effect of water is to divert part of the photoassisted reaction from production of CO to production of formic acid. However, the data provide no mechanistic inferences and do not provide a basis for concluding whether CO is a precursor of formic acid.

4.5. Comparison of Equilibrium Conversion with Photoassisted Conversion

The reaction which produces CO is presumably the reverse of the water-gas shift reaction. Observed efficiencies for the conversion of CO_2 can be compared with fractional conversions calculated from thermodynamic data for the gas phase water-gas shift reaction (*8*). The equilibrium constant calculated for the formation of CO is 1.23×10^{-5} at 30°C. Percent conversions of CO_2, calculated from this value, are compared in Table 3 with conversion efficiencies obtained with the most active catalyst employed, Co-Mo-Al-oxide. No effort was made to establish equilibrium in the dark reaction or to achieve the photostationary state under illumination. Nevertheless, the fact that photoassisted conversion efficiency exceeds the value calculated for gas phase equilibrium, and by a factor of about 10 in the presence of added water vapor, suggests that there is a large difference between the dark equilibrium and photostationary states and supports the possibility of obtaining substantially higher efficiencies of conversion of CO_2 and H_2 by manipulation of conditions, e.g., residence time of reactants in the cell and intensity of illumination and area of catalyst surface accessible to light.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

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Received June 18, 1986