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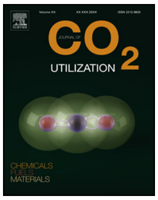

Short communication

Photocatalytic reduction of CO_2 under supercritical CO_2 conditions: Effect of pressure, temperature, and solvent on catalytic efficiency

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ABSTRACT

The photocatalytic reduction of CO_2 to CO in single-phase, high-pressure mixtures of supercritical CO_2 and *N*,*N*-dimethylformamide (DMF), using *fac*-ReCl(bpy)$(CO)_3$ as a catalyst in the presence of triethanolamine as a sacrificial electron donor has been investigated. The catalytic efficiency was found to be strongly influenced by both the CO_2 and DMF concentrations. For example, the turnover number (TON) for CO formation increases linearly with CO_2 pressure up to 60 at 17.8 MPa/60 °C. It also increases dramatically as the [DMF] is increased from 3.8 to 6.3 M, and then remains almost constant with further increases in [DMF]. This resulted in an optimized TON of 62 at 17.8 MPa CO_2/60 °C and [DMF] = 6.3 M, and an initial turnover frequency (TOF) of ~56 h^{-1} at 17.8 MPa CO_2/60 °C and [DMF] = 11.4 M. These values are 5× and 2.3× higher, respectively than those obtained under biphasic low-pressure conditions (0.1 MPa CO_2), demonstrating that significant improvements in catalytic performance are possible through the use of high concentrations of CO_2. Manipulation of the incident light intensity led to further improvements in both TON (up to 72 under low light levels) and TOF (up to 117 h^{-1} under the highest light level investigated).

1. Introduction

In recent years, energy sustainability issues have motivated research to develop an effective artificial photosynthetic process using solar energy [1]. Many transition metal complexes based on different metal centers such as Re, Ru, Co, and Ni, have been investigated as homogeneous catalysts for the direct production of carbon monoxide (CO) and/or formate from carbon dioxide (CO_2) [2]. However, extremely low catalyst stabilities and efficiencies have restricted the large-scale application of these processes.

In the early 1980s, Lehn et al. reported the photocatalytic reduction of CO_2 to CO using *fac*-ReX(bpy)$(CO)_3$ complexes ($X = Br^-$ or Cl^-; bpy = 2,2′-bipyridine) as catalysts [3]. Upon visible-light irradiation ($\lambda > 400$ nm) into the metal-to-ligand charge transfer (MLCT) excited state of the catalyst in CO_2-saturated *N*,*N*-dimethylformamide (DMF) solution in the presence of triethanolamine (TEOA), which acts as a sacrificial electron donor to the MLCT state, the selective production of CO was observed with turnover numbers (TONs) [4] of up to 27 in the absence of additional additives [3]. Isotopic labeling studies confirmed that the CO was generated exclusively from CO_2, as opposed to from catalyst or solvent decomposition. While the precise mechanism for the reaction is still under debate, and different byproducts can be generated in addition to CO, it should be noted that a source of protons is always required (see Eqs. (1) and (2) for two of the possible overall reactions). The most likely source of the protons is either residual water in solution, or the sacrificial amine donor, which is known to form a conjugate acid, $TEOAH^+$ after donation of an electron to the catalyst and subsequent reaction with another molecule of TEOA.

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \tag{1}$$

$$2CO_2 + 2e^- + H^+ \rightarrow CO + HCO_3{}^- \tag{2}$$

Since the original report [3a], many *fac*-ReX(bpy)$(CO)_3$ complexes have been shown to catalyze the reduction of CO_2 to CO, with quantum yields for the formation of CO as high as 0.59 [5]. However, the TONs are still not high enough for practical photocatalytic conversion of CO_2 due to the formation of non-productive side products. Turnover frequencies (TOFs) [4] are also extremely low (on the order of ~1–12 h^{-1}) [2b], since some of the dark reactions that follow light absorption and reductive quenching of the catalyst have extremely low rate constants [6]. For a formal definition of TON, TOF and TOF_{init}, as used throughout this paper, see Ref. [4].

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In efforts to improve the catalytic efficiency, previous investigations have focused on ligand modifications, either by replacing the bpy and/or peripheral ligands, or through the introduction of different substituents on the bpy ligand to manipulate the electronic properties of the catalyst [5b,7]. Ishitani et al. have also demonstrated significant improvements through the use of supramolecular systems consisting of a visible-light absorbing $Ru(dmb)_3^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) photosensitizer unit covalently linked to a Re-based catalytic unit [2d]. An alternative approach, however, is to make use of high concentrations of CO_2 using elevated CO_2 pressures (liquid or supercritical CO_2 ($scCO_2$)) as a means to accelerate the reaction of the reduced catalyst with CO_2 and to minimize the extent of side reactions. Hori et al. investigated the use of high-pressure CO_2 gas with *fac*-$ReCl(bpy)(CO)_3$ in DMF with triethylamine (TEA) as an electron donor, and found that the TON for CO production increased from 8.2 at 0.1 MPa CO_2 to 41.8 at 2.45 MPa [8]. Although this shows the effectiveness of pressurized conditions, all of the experiments were conducted under biphasic gas–liquid reaction conditions, in which there is a possibility of mass transfer limitations due to the existence of a gas–liquid phase boundary. To overcome this type of situation, $scCO_2$ has often been used as an alternative medium for chemical reactions and syntheses, resulting in higher reaction rates [9]. $ScCO_2$ (ρ_c = 10.6 M (or 0.47 g cm^{-3}), P_c = 7.4 MPa, T_c = 31.0 °C) offers many advantages because of its easily tunable properties of viscosity and polarity, *etc.*, and its high CO_2 density (*i.e.*, $[CO_2]$). In particular, the ability to tune the CO_2 density over a wide range simply by changing pressure and temperature, and the phenomenon of local density enhancement in $scCO_2$ [10], might provide great potential for overcoming the disadvantages associated with the low TON in the photoreaction process. We should note that $scCO_2$ has been shown to enhance the efficiency of photocatalytic CO_2 reduction for a catalytic system consisting of $Ru(bpy)_3^{2+}/[Ni^{II}(cyclam)]^{2+}$/ascorbate as photosensitizer/catalyst/sacrificial electron donor, respectively in a water–$scCO_2$ biphasic system [11]. However, in that case all reactants are dissolved in the water phase and CO_2 from the $scCO_2$ phase interacts with a $[Ni^{I}(cyclam)]^{+}$ catalytic intermediate at the water–CO_2 interface.

We have previously developed Re complexes with fluorinated substituents on the bpy rings to induce high $scCO_2$ solubility [2b,12]. However, the TONs obtained when these were tested for photocatalytic CO_2 reduction in pure $scCO_2$ in the presence of TEA were low. Hori et al. also found similarly low TONs in their investigation of [*fac*-$Re(bpy)(CO)_3P(OC_6H_{13})_3]^+$ in single-phase liqCO_2/TEA [13]. In a later publication investigating CO_2 reduction with [*fac*-$Re(bpy)(CO)_3P(O^iPr)_3]^+$ in DMF/TEA with both CO_2(g) and liqCO_2 [14], it was suggested that the presence of a separate CO_2 gas phase at high pressures may be important to obtain good TONs, since it would prevent the build-up of CO around the active catalyst. However, neither $scCO_2$ nor the better sacrificial electron donor, TEOA were investigated, and the concentration of DMF used in the single-phase liqCO_2 experiment (at 7.3 MPa, 26 °C) was low (~2 M). Thus, in the present study we have investigated the photocatalytic reduction of CO_2 with *fac*-$ReCl(bpy)(CO)_3$ under high-pressure, single-phase $scCO_2$ conditions in the presence of an organic solvent component (DMF), with TEOA as an electron donor. The aim was to determine if efficient reduction of CO_2 to CO can be achieved in a single-phase $scCO_2$ environment, and to establish how the different reaction parameters (*i.e.*, CO_2 pressure, temperature, DMF concentration, and incident light intensity) influence catalytic performance. This resulted in an optimized TON of 62 and TOF_{init} of 56 h^{-1} at 17.8 MPa CO_2/60 °C, both of which are high values for this catalytic system compared to those obtained under ambient CO_2 pressures under our experimental conditions. Finally, manipulation of the incident light intensity led to a maximum TON of 72 at low light levels, while the TOF increased linearly with light intensity (up to 117 h^{-1} over the range investigated) at the expense of the TON.

2. Experimental

The experimental apparatus for high-pressure photocatalytic CO_2 reduction is shown in the supplementary data (Fig. S1). The solvent phase behavior was first confirmed in the high-pressure cell containing DMF/TEOA at 60 °C. It was found that a single phase was attained when the $scCO_2$ pressure was $\geq$11 MPa (see Fig. S2). All CO_2 reduction experiments were performed with photolysis light in the 370–550 nm range. More experimental details can be found in the supplementary data.

3. Results and discussion

CO_2 reduction was initially performed under biphasic low-pressure conditions in DMF (0.1 MPa CO_2, 40 °C). A TON of 12 was obtained after 200 min of irradiation, which is similar to that previously reported for this system [3a]. Upon increasing the pressure to 13.8 MPa of $scCO_2$ (single-phase conditions), the TON was enhanced by 1.4 times (TON of 17 *vs.* 12, see Table 1, runs 1 and 2), while the time taken for complete catalyst decomposition decreased to 50 min. Thus, under these conditions, the overall TOF was enhanced in $scCO_2$ by ~5× relative to ambient pressure (20 *vs.* 4 h^{-1}). The effect of temperature on the catalytic efficiency under $scCO_2$ conditions was also investigated from 40 to 70 °C, at a constant CO_2 density of 5.5 M (Table 1, runs 3–6). Over this temperature range (which involves an increase in pressure from 13.2 to 26.0 MPa), the TON remained almost constant within experimental error (±5), with catalyst decomposition occurring in ~50 min in each case. In contrast, under constant pressure conditions (13.8 MPa), upon increasing the reaction temperature from 40 to

Table 1

Turnover numbers for the production of CO upon irradiation ($370 \leq \lambda \leq 550$ nm) of *fac*-$ReCl(bpy)(CO)_3$ in DMF/CO_2 in the presence of TEOA under different reaction conditions [4]. [*fac*-$ReCl(bpy)(CO)_3$] = 0.58 mM.

Run	T (°C)	P (MPa)	[DMF] (M)	$[CO_2]$[a] (M)	CO_2 state	TON
1[b]	40	0.1	12.9	0.13[d]	Gas	12
2[c]	40	13.8	7.5	5.7	$scCO_2$	17
3[c]	40	13.2	7.5	5.5	$scCO_2$	17
4[c]	50	17.4	7.5	5.5	$scCO_2$	26
5[c]	60	21.7	7.5	5.5	$scCO_2$	20
6[c]	70	26.0	7.5	5.5	$scCO_2$	28
7[c]	50	13.8	7.5	4.9	$scCO_2$	26
8[c]	60	13.8	7.5	4.0	$scCO_2$	52
9[c]	70	13.8	7.5	3.3	$scCO_2$	24
10[c]	60	10.5	7.5	2.4	$scCO_2$	38
11[c]	60	13.5	7.5	3.9	$scCO_2$	48
12[c]	60	17.8	7.5	5.0	$scCO_2$	60
13[c]	60	20.6	7.5	5.4	$scCO_2$	47
14[c]	60	24.2	7.5	5.7	$scCO_2$	32
15[c]	60	17.8	3.8	9.5	$scCO_2$	8
16[c]	60	17.8	6.3	6.5	$scCO_2$	62
17[c]	60	17.8	9.1	3.1	$scCO_2$	53
18[c]	60	17.8	11.4	0.3	$scCO_2$	50

[a] $[CO_2]$ was estimated by taking into account the volume of DMF and TEOA inside the cell and assuming these to be incompressible, then calculating the amount of CO_2 in the remaining volume using the NIST Standard Reference Data [15], and then calculating the $[CO_2]$ based on that CO_2 occupying the total cell volume under single-phase conditions. Note that this procedure results in considerably lower values of estimated $[CO_2]$ compared to a simple calculation of $[CO_2]$ based on the temperature and pressure of pure CO_2 occupying the cell in the absence of DMF and TEOA.

[b] [TEOA] = 1.24 M.

[c] [TEOA] = 0.72 M.

[d] Concentration of CO_2 dissolved in the DMF phase under biphasic conditions [16].