Influence of Reaction Reaction Medium on Photocatalytic CO2 Reduction

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Abstract. A comprehensive investigation is carried out on the photocatalytic reduction of CO2 in various reaction mediums, including conventional organic solvent, ionic liquid, and water. Different photocatalytic activity could be achieved by altering the solvent molecules in the liquid photocatalytic system. The catalytic performance depended on the amount of CO generation in the system, suggesting that the properties of solvent are depended on the amount of CO generation in the system, suggests that the properties of solvent are closely associated with the formation of intermediate. The affecting factor on the stabilization of CO2 is the transition in solution, which is related to the changes in the interaction strength of each ingredients.

1. Introduction

Renewable and sustainable energy source is highly desirable for solving the serious environmental burdens and energy shortage problems[1]. In this topic, photocatalytic CO2 fixation has attracted worldwide attention due to its potential in carbon recycling and solar energy conversion. By using an efficient photocatalyst, sunlight can be converted to chemical energy to achieve value-added chemicals, such as CH4, CO, CH3OH, and CnH2n+2 etc[2].

Since the initial report on photocatalytic CO2 reduction, various photocatalytic systems have been explored to realize photocatalytic CO2 reduction[3]. All these systems are generally classified into two categories: one is gas-solid photocatalytic system and the other is gas-liquid-solid/gas-liquid system[2-3]. Liquid systems takes a dominant number based on laboratory works, which is typically preferable to former in terms of good efficiency, high quantum yields and environmental interest. In other words, the reported heterogeneous and homogeneous photocatalytic CO2 reduction systems are mainly operated in liquid phase (e.g., suspension or solution). Therefore, it calls for the understanding of the relationship between the photocatalytic performances and the nature of reaction medium.

It is known that the first step in CO2 conversion involves the formation of a “CO2-” intermediate, which requires a high reaction potential (e.g., -2.2V vs. SCE, in DMF solution)[4]. Previous studies demonstrate that the properties of used solvent can obviously decrease the energy barrier during CO2 activation. For instance, using 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF4) as reaction medium, the generation of CO2- anion only need a much lower over potential of 0.17 V due to the complex effect of EMIM+[5]. Besides, it is also reported that the selectivity of CO2 reduction is mainly depended on the adsorption of CO2- on catalyst surface, which is also largely affected by the nature of reaction solvent. Additionally, the solvent-dependent and charge-transfer equilibrium between active radicals is explored in organic synthesis[6].
Herein, we conducted an intensive study on the influences of solvent molecules to CO2 activation and conversion, which is of particular importance but rarely reported. We demonstrate an investigation of solvent effects on the performance of photocatalytic CO2 reduction. Three categories of reaction medium including conventional organic solvent, ionic liquid and water has been selected, and the relationship between photochemical CO2 performance and the categories of reaction medium are discussed in this paper. Moreover, a possible reaction mechanism involving photoexcited charge transfers and intermediate species transformations in various solvents is proposed.

2. Experiments
All experiments were performed in a Schlenk flask (80 ml) under an atmosphere pressure of CO2 (1 atm)[7]. For conventional organic solvents: CdS (50 mg), 2, 2'-bipyridine (15 mg), CoCl2·6H2O (10 μmol) were added in the mixture of solvent (5 ml) and triethanolamine (TEOA, 1 ml). The system was subjected to vacuum degassing and back filling with pure CO2 gas. This process was repeated three times, and after the last cycle the flask was back filled with CO2. Then the system was irradiated with several 150 W white LED under vigorous stirring at 20 oC and controlled by a water-cooling system.

3. Result and discussion
The influence of solvent on chemical equilibrium has long been investigated, and can be mainly measured by dielectric constants[6]. Additionally, the solvent-dependent, charge-transfer equilibrium between active radicals is explored as well in organic synthesis. Based on our previous work, different kinds of reaction medium employed in the photocatalytic CO2 have been investigated.

3.1. Conventional solution
It is reported that the activity and selectivity of CO2 reduction is mainly depended on the adsorption of CO2- on catalyst surface, which is also largely affected by the nature of reaction solvent. In low polar solvents, the formed CO2- may be adsorbed strongly to the active surface sites of photocatalyst by carbon atom of the anion. In this case, carbon monoxide and formate are usually the main products. Alternatively, the CO2- anion is prone to be stabilized by the solvent molecules with high dielectric constant, resulting in weakened interaction with photocatalyst, and thus generating formate as the product[4]. On the other hand, the CO2- anion would form a M-CO2- (M = metal) intermediate as the first reaction step in metal-containing CO2 reduction systems, and the properties of reaction solvent are considered to be of crucial importance to the generation and stabilization of M-CO2- adducts [8].

Fig.1. Production of CO and H2 in different solvents: (a) MeCN, (b) DMF, (c) THF, (d) DMSO, and (e) H2O
The above analysis are determined by the time courses of products in different solvents. As shown in Figure 1, the reaction rate of CO2 reduction catalysis is largely determined by the properties of used solvents. When the reaction is performed with MeCN as the solvent, the catalytic system manifests the highest production of CO and H2. Using H2O as the reaction solvent, the production of CO is negligible, but the evolution rate of H2 nearly maintains at constant. This observation is reasonable as the presence of plentiful protons facilitates H2 generation. These findings further demonstrate that the properties of solvents (such as solubility, viscosity and coordination etc.) in the system greatly influences the performance of CO2 photoreduction.

3.2. Ionic liquid

Ionic liquids are room temperature molten salts, which are formed by the weak combination of a large organic ion and a charge-delocalized inorganic/organic anion with versatile structural and functional variations[9]. The scientific and technological importance of ionic liquids is their wide applications in lubricants, electrolytes, catalysts and as gas capturer[10]. The advantages of ILs are the promising application of ILs as green solvents with a number of important properties, such as negligible volatility, high stability, high ionic conductivity, high polarity, and solubility with many compounds[11]. Interestingly, in the above-mentioned carbon capture systems, the formation of carbamates is evident by binding of CO2 either to the amines tethered to cations (or anions) of ILs or to the amino groups. This way is similar to the first step of plant photosynthetic cycle, in which the CO2 molecule is initially bonded to nitrogen atoms, making reactive carbamate intermediates in the biology system[12]. We are therefore inspired to link the unique coordination chemistry of ILs to artificial photosynthesis for promoting carbon fixation. The system cooperatively works with ILs to accelerate CO2 photochemical reduction in various solvents at mild conditions.

Fig. 2. The promotional effect of ILs on CO2 photofixation in various solvents (DMF: N,N-dimethylformamide. MeCN: acetonitrile. THF: tetrahydrofuran. BTF: benzenyltrifluoride).

The IL-promoted CO2 photoreduction system was then carried out in various reaction media to determine the generality of the promotional effect of ILs and also to search for a favorable IL-coupler as reaction medium for efficient CO2 photofixation. Various solvents were applied in the CO2 reduction system. The corresponding results are shown in Figure 2. Remarkably, upon adding [EMIM][BF4], all solvent systems displayed enhanced photocatalytic reactivity towards CO2 reduction to various extents. In the IL-MeCN mixture, the CO evolution rate reached 25μmol/h.

3.3. Water

Most of the research on CO2 photoreduction was related to using water as reaction medium or/and aqueous H+ source (H2O+hVB+= [O] +2H+).[13] That is, proton-coupled multi-electron steps for CO2 reductions are generally more favorable than single electron reductions, as thermodynamically more stable molecules are produced and the large reorganization energy between the linear molecule
and bent radical anion is therefore lowered.[14] Of note, the choice of environmental friendly solvent of water is of great interest because it can serve as a simple model for green synthetic methods. Recently, we found that the reaction medium (MeCN/TEOA) with proper ratio of water divides into two phase during reaction, which is likely related to the efficiency of photocatalytic CO2 reduction.

![Graph](image)

**Fig. 3** Effect of the water concentration on the evolution of CO/H2 in H2O-MeCN system

In addition, a comprehensive investigation has been conducted to uncover the mechanism of promotional effect from water on the photocatalytic activity of CO2 reduction. We presented a binary liquid system in the typical photocatalytic CO2 reduction reaction by adding water. As shown in Figure 3, the generation amount of CO reached 89μmol in MeCN solution with additive 30% water, which is much higher than that in MeCN (16 μmol) or H2O (1.6 μmol) as reaction medium, respectively. This novel system exhibits high photocatalytic reactivity towards CO2-to-CO conversion due to the addition of water as another phase promoting charge-carrier separation, transfer kinetics, and interface interaction. It should be noted that the excellent photocatalytic activity in binary liquid phase can be developed as an universal photocatalytic CO2 reduction system. This finding clearly indicates that the integration of water with various organic solvents is a feasible process for the design and development of efficient photochemical systems for CO2 conversion.

### 4. Conclusion

In summary, we have demonstrated the systematic study of photocatalytic CO2 reduction catalysis occurring in various reaction mediums. The properties of solvent in CO2 photochemical reduction are strongly related to the chemical properties of organic functional groups on the solvent molecules and the volume ratio of solvent. Solvent chemistry thereby continues to facilitate new strategies for the creation of valuable chemicals from CO2 by photoredox organocatalysis. This new photochemical cascade reaction offers a new understanding to split and convert chemically inert CO2, by the extension of reaction medium to artificial photosynthesis.

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