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Selective photoreduction of CO_2 to CO in CO_2-dissolved expanded liquid phase with heterogeneous CO_2-philic Pd complex catalysts

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ABSTRACT

Novel CO_2-philic Pd complexes, $PdCl_2$[4,4'-bis($R_fCH_2OCH_2$)-2,2'-bpy] (bpy: 2,2'-bipyridine) where R_f = *n*-$C_{10}F_{21}$, *n*-$C_{11}F_{23}$, were anchored onto a silica support modified with long fluorinated hydrocarbon chains (C_6F_{13}) by mixing these complex and the support in DMSO at 413 K. These immobilized Pd complex catalysts were applied for the photoreduction of CO_2 in DMF or organic solvents using triethylamine as a hydrogen donor at 323 K. The rate of CO_2 reduction and the selectivity to CO were observed to depend on several factors including CO_2 pressure, solvent, Pd complex structure, and Pd loading. With the most active catalyst, the selective photoreduction of CO_2 to CO can be achieved in DMF at a CO_2 pressure of 4 MPa and the performance observed is much better compared to the literature results. The features of the supported

Pd complexes and the multiphase reaction media were characterized by UV-Vis absorption and others to discuss the reasons for their high performance.

Keywords:

Heterogeneous catalysis; Palladium; Reduction; Catalyst design; Photocatalysis; Expanded liquid

1. Introduction

The photochemical transformation of CO_2 into valuable organic compounds and fuels has grown into an intense area of research owing to the global warming problem and the fossil fuels shortage [1,2]. The photocatalytic reduction of CO_2 using photosensitive transition metal complexes has widely been investigated in homogeneous systems because metal complexes have high quantum efficiency and selectivity for the production of carbon-containing species, relative to semiconductors [3-6]. The photoreduction of CO_2 with metal complexes have extensively been performed in organic solvents at room temperature and ambient pressure with a sacrificial electron donor such as triethanolamine (TEOA) and triethylamine (TEA) [7,8] However, the catalytic performance observed so far is still low and one of possible reasons is the limited concentration of CO_2 in organic solvents under the conditions used. The solubility of CO_2 in conventional organic solvents is typically on the order of 0.1-0.3 M under ambient conditions [9]. The concentration of CO_2 plays a significant role in determining the rate of photoreduction of CO_2. It was reported that when $Re(bpy)(CO)_3Cl$ complex was used, a key intermediate of $Re(bpy)(CO)_3(CO_2)$ complex for the production of CO was shown to decay with a first-order dependence on the

concentration of CO_2 [10]. An obvious approach to overcome the problem of low CO_2 concentration is to perform the reactions at high pressures.

The pressurization of a conventional organic solvent with a high pressure CO_2 will result in an increase in the concentration of CO_2 in the liquid phase and an expansion of its volume. Such a liquid phase is called as a CO_2-dissolved expanded liquid phase (CXL) [11]. In recent years, CXLs have been recognized as an innovative and ecologically benign reaction media for chemical synthetic reactions [12,13]. This is because CXLs have several advantages including high miscibility of metal complexes and gaseous reactants such as H_2, O_2, and CO, high diffusion rate, low viscosity, and tunable solvent properties changing from neat organic solvents through supercritical carbon dioxide ($scCO_2$) [14]. These properties may easily be varied by CO_2 pressure. In addition to those physical impacts, dense phase CO_2 can also have chemical effects on organic reactions through molecular interactions with substrates, intermediates, and catalysts [15,16]. Those attractive features of CXLs as promising reaction media are demonstrated in review articles [17,18]. For example, the authors have revealed the chemical function of dense phase CO_2 in CXLs for hydrogenation, oxidation, hydroformylation, acid-catalyzed reaction, Heck reaction, and Diels-Alder reaction [19]. However, only a few reports have been focused on photochemical CO_2 reduction in CXLs even in dense phase CO_2 systems [20-28]. Mizuno et al. studied the photoreduction of high pressure CO_2 with TiO_2 powder in aqueous solution [23-26]. They found that an increase in CO_2 pressure significantly accelerated the CO_2 reduction and improved the CO_2 reduction selectivity [23]. In 2000, Hori et al. gave the first example of photochemical reduction of CO_2 to CO by CO_2-soluble rhenium phosphite complexes such as $[Re(bpy)(CO)_3\{P(OC_6H_{13})_3\}][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ in liquid CO_2 [27]. The turnover number for CO formation at a CO_2 pressure of 1.36 MPa was 3.8

times larger compared to that for the photoreduction of CO_2 using [*fac*-Re(bpy)$(CO)_3P(O^iPr)_3]^+$ at ambient pressure. They pointed out that the high CO_2 concentration enhanced the reaction of one-electron-reduction catalytic species with CO_2 and prevented the deactivation of the catalyst [28]. Those observations have stimulated us to study the photoreduction of CO_2 to CO in CXLs by using Pd complexes of CO_2-philic nature.

In the present work, CO_2-philic Pd complexes anchored on a silica support were used for the photoreduction of CO_2 in CXLs using dimethylformamide (DMF) and other solvents. Novel CO_2-philic Pd complexes, $PdCl_2$[4,4'-bis($R_fCH_2OCH_2$)-2,2'-bpy] (bpy: 2,2'-bipyridine) where, R_f = *n*-$C_{10}F_{21}$ and R_f = *n*-$C_{11}F_{23}$, were prepared and then anchored (immobilized) onto a silica support modified with long fluorinated hydrocarbon chains. The immobilized Pd complex catalysts prepared were shown to be very active for the selective photoreduction of CO_2 to CO in DMF using TEA as a sacrificial agent, compared to the previous reactions reported in the literature. A high turnover frequency of 65 h^{-1} was obtained for the selective production of CO from CO_2 reduction at 323 K with a catalyst in which the Pd complex of R_f = *n*-$C_{11}F_{23}$ was loaded in 2 wt% onto the fluorinated SiO_2 support. The immobilization of the fluorinated Pd complexes onto the fluorinated support improves their CO_2 photoreduction activity, CO selectivity, and stability, compared to the free Pd complexes, which were observed to change into metallic Pd particles during the reaction. Several variables determining the rate of CO_2 reduction and the CO selectivity have been studied, including CO_2 pressure, structure of Pd complex, loading of Pd complex, and organic solvent.

2. Experimental Section

2.1. Catalyst Preparation and Characterization

The synthesis of fluorinated Pd complexes, $PdCl_2$[4,4'-bis($R_fCH_2OCH_2$)-2,2'-bpy] (bpy: 2,2'-bipyridine) where, R_f = *n*-$C_{10}F_{21}$ and R_f = *n*-$C_{11}F_{23}$, was reported elsewhere [29,30], which will be abbreviated as Pd-F_{21} and Pd-F_{23}, respectively, in the following. A fluorinated silica support, silica gel 60 C_8-reversed phase perfluorinated (synonym: perfluorinated silica gel 60), was purchased from Fluka. This silica support will be abbreviated as F-SiO_2. The size of silica particles was in the range of 0.035-0.070 mm.

The Pd complexes were anchored onto the fluorinated silica as follows. A 2 wt% Pd-F_{21} supported sample was prepared by dissolving 5 mg Pd-F_{21} and 250 mg support in 2 cm^3 DMSO. The whole solution was stirred at about 140 ºC for several hours and then the temperature was cooled down to room temperature, yielding a light yellow solid anchored on the fluorinated silica surface. This sample indicated FTIR (Perkin Elmer RXI FTIR spectrometer) absorption bands of 1625.6 w (*ν* bpy), 1550.0 w (*ν* bpy), 1258.0 vw (*ν* CF_2) and 1097.1 w (*ν* CF_2). A sample of 2 wt% Pd-F_{23} on F-SiO_2 was prepared by dissolving 2 mg Pd-F_{23} and 100 mg support in 2 cm^3 DMSO, followed by the same procedure as for Pd-F_{21}/F-SiO_2. The resulting yellow solid sample showed FTIR absorption bands (those only shown for anchored Pd-F_{23} but not for F-SiO_2) at frequencies (cm^{-1}) of 1627.6 w (*ν* bpy), 1447.0 w (*ν* bpy), 1218.0 vw (*ν* CF_2) and 1089.4 w (*ν* CF_2). Other 10 wt% supported Pd complex samples were also prepared in similar procedures.

The samples of Pd-F_{21} and Pd-F_{23} on F-SiO_2 prepared were examined by field emission scanning electron microscopy (SEM, JEOL 6335F) equipped with an energy dispersive X-ray (EDX) analysis. The unsupported and anchored fluorinated Pd

complexes were also examined by diffuse reflectance UV/Vis absorption measurements with a Shimadzu UV-3100PC spectrophotometer. $BaSiO_4$ was used as a reference and the absorption spectra were obtained by using the Kubelka-Munk function.

2.2 Photoreduction of CO_2

Using those supported and free fluorinated Pd complex catalysts prepared, the reaction runs were carried out in a laboratory designed high pressure stainless steel reactor of 50 cm^3 with a quartz window (diameter 1 cm). In a typical run, a catalyst (20 mg), an organic solvent (10 cm^3) and triethylamine (TEA, 2 cm^3) were introduced into the reactor. The reactor was flushed with 1 MPa CO_2 three times to remove air. The reactor was placed on a heating plate and wrapped by a heating tape. The temperature was monitored by a thermocouple embedded in the reactor wall. The reactor was heated while stirring by a magnetic stirrer. When the temperature reached to 323 K, CO_2 was introduced up to the desired pressure. The reaction mixture was illuminated by a 500 W high-pressure Hg lamp (Ushio USH-500SC). This lamp emits the light predominantly in the wavelength range of 360-370 nm, 400-410 nm, and 430-440 nm. After the reaction, the pressure was reduced carefully by a back pressure regulator and the gases (CO_2, CO, CH_4, H_2) evolved were collected in a gas trap. The amounts of CO, CH_4, and CO_2 were determined by a gas chromatograph (Shimadzu GC-8A, Porapak Q packed column, FID detector, N_2 carrier) with a methanizer converting those gases into CH_4, and that of H_2 by a gas chromatograph (Shimadzu GC-8A, molecular sieve 5A packed column, TCD detector, N_2 carrier). The liquid phase was analyzed by a gas chromatograph (Shimadzu GC-14B, Porapak T packed column, FID detector, He carrier). Under the reaction conditions used, no other hydrocarbons such as HCOOH, CH_3OH and HCHO were

detected. For comparison, a physical mixture of the Pd complex and the F-SiO_2 support was tested for the CO_2 photoreduction. The complex and the support were charged into the reactor with DMF and TEA. After the mixture was stirred for 30 min at room temperature, the reactor was heated to the reaction temperature and then introduced with CO_2 at the desired pressure in the same manners as above-mentioned.

2.3. Phase behavior observation

The phase behavior is one of important factors determining the reaction rate and the product selectivity for multiphase reactions. It was examined by visual observation using an autoclave with a transparent glass window. A certain volume of organic liquid was added to the autoclave for the liquid/autoclave volume ratio to be similar to that used in photoreduction of CO_2 reaction runs. The autoclave was heated to 323 K (reaction temperature) and CO_2 was introduced to the desired pressure under stirring. The phase behavior was visually examined in different solvents at different CO_2 pressures.

3. Results and discussion

3.1. Catalysts Prepared

Heterogeneous Pd catalysts were prepared using fluorinated Pd complexes and silica support modified with long fluorinated hydrocarbon chains (F-SiO_2). The fluorinated Pd complex was anchored onto the F-SiO_2 support by mixing a solution of the complex in DMSO with F-SiO_2 support at 413 K as shown in Fig. 1. Yellow and

light yellow powder samples were obtained with Pd-F_{23} and Pd-F_{21}, respectively, and the DMSO solvent was clear, indicating that the Pd complexes were successfully anchored onto the F-SiO_2. The catalysts were prepared from Pd-F_{21} and Pd-F_{23} complexes different in the length of fluorinated tail with a Pd loading of either 2 wt% or 10 wt%.

Fig. 1

The Pd-F_{21} and Pd-F_{23} anchored F-SiO_2 were examined by SEM-EDX. The results obtained are given in Supplementary Information. The EDX analysis results clearly show that both Pd-F_{21} and Pd-F_{23} complex are immobilized onto F-SiO_2 support. It was also observed that the percentage of either F or Si atoms accounted for *ca* 50% and that of either Pd or Cl atoms only accounted for less than 1 %.

Fig. 2 shows the diffuse reflectance UV-Vis spectra for unsupported and anchored fluorinated Pd complexes. The unsupported Pd-F_{21} and P-F_{23} complexes exhibit almost the same absorption bands in the high-energy region (λ <350 nm) but the absorption intensity of the former is a little stronger than that of the latter (Fig. 2A). A high energy absorption band at round 260 nm is assigned to the π-π^* transition introduced by the bipyridine moieties. Another absorption band at ~310 nm and weak intense low-energy band around 360-420 nm may be ascribed to spin-allowed metal-to-ligand charge transfer (MLCT) transitions that involve a Pd 5d π orbital as the donor orbital and a π^* bipyridine orbital as the acceptor orbital. No absorption is observed for the fluorinated silica alone (Fig. 2B-a). The main absorption bands of 2 wt% Pd-F_{21}/F-SiO_2 and 2 wt% Pd-F_{23}/F-SiO_2 are blue shifted by about 15 nm and the intensities of these absorption bands are stronger compared with the spectra of the free complexes. When the Pd loading is raised to 10 wt%, the main absorption band is

further blue shifted for the supported Pd-F_{23} sample but not changed for the Pd-F_{21} sample. The long wavelength absorption is extended to 600 nm for the supported Pd complexes from 380 nm for the free samples. Those changes in the UV-Vis spectra indicate the presence of interactions of the Pd complexes with the F-SiO_2 support through its long fluorinated tails, which may modify their photocatalytic activities, as described later.

Fig. 2

3.2. Photoreduction of CO_2 with a Pd-F_{23}/F-SiO_2 Catalyst

The CO_2 photoreduction was examined with 2 wt% Pd-F_{23}/F-SiO_2 using TEA as sacrificial agent in the presence of dense phase CO_2 and/or an organic solvent of DMF. Table 1 show the results obtained under different conditions (in different reaction systems as illustrated in Fig. 3). In all cases, CO, a two-electron reduction product of CO_2, was mainly formed with a small amount of H_2 from the sacrificial agent. In DMF/TEA solution under ambient CO_2 pressure (entry 1), which is a widely used reaction system in the literature, the rate of CO production was 14.8 h^{-1}. When a high CO_2 pressure of 4 MPa was used in the absence of DME, a larger CO_2 production rate of 41.5 h^{-1} was observed (entry 2). In this case, CH_4, an eight-electron reduction product, was also produced at a rate of 5 h^{-1}, along with H_2 at a rate of 8.8 h^{-1} from TEA due to the electron donor-acceptor interaction between CO_2 and TEA [31]. It is noteworthy that the CO production rate was enhanced to 65.8 h^{-1} in the presence of DMF as well (entry 3), in which no CH_4 was detected and the H_2 production was also suppressed. A large amount of CO_2 is soluble in DMF at a pressure of 4 MPa, producing an expanded

liquid phase (Fig. 3c). The CO_2 concentration is large and the liquid phase is more CO_2-philic, which is favorable for promoting the CO_2 reduction and allowing the CO_2-philic Pd complex to work more effectively. According to the literature [28], the concentration of CO_2 in a similar DMF/TEOA solution at 5.57 MPa was 12.5 M, about 95 times higher than that at ambient pressure. It is assumed that the concentration of CO_2 in the DMF/TEA solution is much larger due to the stronger electron donor-acceptor interaction with more basic TEA relative to TEOA [28,31]. Table 1 indicates that a higher CO_2 pressure of 8 MPa decreases the rate of CO production (entry 4). At 8 MPa, the liquid phase of DMF and TEA are soluble and diluted in the dense phase CO_2 and this is a significant reason for the lowered rate of CO production of 11.0 h^{-1}. Thus, the reaction system including both DMF and CO_2 at a medium pressure is beneficial for the photoreduction of CO_2 to CO, which is illustrated in Fig. 4.

Table 1, Fig. 3

The influence of CO_2 pressure was further studied for the reaction system of Fig. 4. The rate of CO production was strongly dependent on the pressure, as shown in Fig. 5, which was largely enhanced by three times with increasing pressure up to about 4 MPa. The CO production markedly decreased when the CO_2 pressure went over 4 MPa. A marginal amount of H_2 was also detected and simply decreased with CO_2 pressure up to 10 MPa, in contrast to the change of CO production. The phase behavior observations at different CO_2 pressures indicate that the volume of the DMF/TEA liquid mixture was expanded with increasing pressure, which was 1.8 times larger at 4 MPa compared with the volume at ambient pressure. The liquid and gas phases were observed to change into a single phase with a small further increase in the pressure. One can say, therefore, that the raising CO_2 pressure is positive for enhancing the CO_2

photoreduction to CO for the CO_2-dissolved expanded liquid phase but negative for the single fluid phase.

Fig. 4, Fig. 5

Furthermore, the authors tested other organic solvents as well, including *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and acetonitrile (MeCN). The results of CO_2 photoreduction obtained with these solvents are given in Table 2. DMF was the best solvent with which the CO production rate was 65.8 h^{-1} with no CH_4 formation (entry 1). With either NMP or THF, the rate of CO production was less than 1/2 of the rate with DMF and the CO selectivity was about 70% (entries 2, 3). The rate of photoreduction of CO_2 with MeCN was even smaller compared to the other solvents and the reaction was more selective to CH_4 than CO (entry 4). When these solvents were pressurized by CO_2, their volumes were observed to expand to a similar extent; the volume of a mixture of solvent and TEA (solvent vs. TEA volume ratio of 5) increased by about 60% at a CO_2 pressure of 4 MPa. Here, the authors will further discuss the results of Table 2 using one of solvent polarity parameters, Reichardt $E_T(30)$ value [32]. The $E_T(30)$ of dense phase CO_2 at 353 K and at 0.5 g cm^{-3}, for example, is around 31.5 kcal mol^{-1} [33]. One can say that, phenomenally, a large rate of CO_2 photoreduction to CO is achieved in a solvent of which $E_T(30)$ value is close to $E_T(30)$ of CO_2 (entry 1); DMF has an $E_T(30)$ of 30.6 kcal mol^{-1}. Such an organic solvent may be suitable for the effective actions of both a CO_2-philic catalyst and a reactant of CO_2. In smaller $E_T(30)$ solvents of NMP (28.2 kcal mol^{-1}) and THF (16.4 kcal mol^{-1}), the overall rate of CO_2 conversion and the selectivity to CO were both lowered (entries 2, 3). In MeCN having an $E_T(30)$ of 36.5 kcal mol^{-1}, the rate and the selectivity were markedly decreased (entry 4). When the solvent properties become less CO_2-philic (dense phase CO_2-like), the rate

of catalytic CO_2 conversion is assumed to decrease due to less effective actions of the catalyst and CO_2 molecules. At present, no explanation is given for the change of the product selectivity. The structure of a reaction intermediate complex including Pd catalyst, CO_2, and TEA would depend on the properties of a solvent used.

Table 2

3.3. Comparison between Supported and Unsupported Pd-F_{23} and Pd-F_{21} Complexes

Under standard conditions using DMF, TEA, and 4 MPa CO_2, immobilized (anchored) and unsupported Pd-F_{23} and Pd-F_{21} complexes were compared in the performance for the photoreduction of CO_2. The comparison was made by using the same amount (1.5 μmol) of Pd complexes used for the reactions conducted. The results obtained are summarized in Table 3, which shows that CO is the main product with a marginal formation of H_2 from the sacrificial agent for all the reaction runs under the conditions used. The activity of the anchored Pd complex is much higher than that of the unsupported free counterpart for both Pd-F_{23} (entries 1, 3, 7) and Pd-F_{21} (entries 2, 4, 8). The maximum TOF of CO formation (65.8 h^{-1}) was obtained with 2 wt% Pd-F_{23}/F-SiO_2 (entry 1), about 6 times larger than that the unanchored counterpart (entry 7). Among the anchored catalysts (entries 1-4), a smaller loading (2 wt%) and a longer fluorinated tail (Pd-F_{23}) gave a more active catalyst. For the free Pd-F_{23} and Pd-F_{21} complexes, some black Pd particles were observed to form after the reactions and this should be a main reason for their low activities. It was further found that a larger amount of Pd particles was formed at a higher CO_2 pressure of 8 MPa and CO was little detected with the free complexes. For the Pd complexes anchored on F-SiO_2 support,

which was yellow in color, the liquid phase after the reaction runs was clear and no black Pd particles were seen. Thus, the anchored complexes are stably supported on the support and this hinders the Pd complexes from dissolving into the liquid phase and decomposing to metallic Pd particles. In addition, a physical mixture of Pd-F complex and F-SiO_2 was also tested under the same conditions. These physically mixed catalysts indicated larger activities (entries 5, 6) compared with the free complexes but smaller activities compared with the anchored complexes. For the physically mixed catalysts, the liquid phase was changed in color from clear to light grey after the reaction, indicating the formation of a small amount of Pd particles. There might be a possibility, however, that the free Pd complexes became anchored onto the surface of F-SiO_2 during the reaction even at a lower reaction temperature of 323 K (compared to the anchoring at 413 K), which is responsible for the larger activities of the physically mixed catalysts compared to the free complexes.

Table 3

For further checking the stability of the anchored Pd complex, the photoreduction of CO_2 was tested for longer reaction times under the standard conditions with 2 wt% Pd-F_{23}/F-SiO_2. The amount of CO was observed to increase linearly during the reaction up to 48 h (Fig.. 6). After the reaction for 18 h, the catalyst was separated from the reaction mixture and the liquid phase was tested for further reaction. No reaction occurred and no UV-Vis absorption band appeared. These results indicate that no Pd complex is leaching from the surface of F-SiO_2 and the activity of the anchored Pd complex catalysts is durable for the reduction of CO_2.

Fig. 6

To confirm that CO originates from CO_2 photoreduction, blank experiments were made. No carbon species was detected under dark conditions in the presence and absence of catalyst and under light illumination conditions in the absence of CO_2. No CO was detected with F-SiO_2 alone on photoirradiation. All these results indicate that CO is evolved through photoreduction of CO_2 catalyzed by the fluorinated Pd complexes but not originates from the organic components of F-SiO_2.

3.4. Comparison between the Present and Previous Catalysts

There are only a few reports concerned with metal complexes anchored onto solid supports for photoinduced activation and reduction of CO_2 [34-41]. Table 4 shows the comparison among different anchored Pd complexes in the performance for the photoreduction of CO_2 at ambient pressure. Rhenium tricarbonyl diimine complexes are well-known two electron reduction photocatalysts for converting CO_2 to CO. Ishitani et al. synthesized a mesoporous biphenyl-silica (Bp-PMO) anchored *fac*-$[Re(bpy)(CO)_3(PPh_3)]CF_3SO_3$ (Re/Bp-PMO) by co-condensation method [36]. The TOF of CO production was 0.1 h^{-1} with Re/Bp-PMO in MeCN with TEOA as sacrificial agent (entry 1). It was found that the photocatalytic CO evolution from CO_2 was enhanced by a factor of 4.4 compared with the homogeneous complex because Bp-PMO could promote the harvest of light and protect the Re complex against a decomposition by UV irradiation. Hirose and co-workers studied the photoreduction of CO_2 with Ru/Nf-Co complex, in which a photosensitizer of $[Ru(bpy)_3]^{2+}$ was fixed to cation exchange Nafion, and $[Co(bpy)_3]^{2+}$ as a homogeneous catalyst (entry 2) [37]. They pointed out that the lifetime of the partially heterogeneous photocatalyst could be prolonged relative to the counterpart homogeneous metal complex due to retardation of

the decomposition of $[Ru(bpy)_3]^{2+}$. This was because the complex could not move from the ion exchange polymer surface and so dissociation of the ligands was suppressed. Unfortunately, the rate of CO production from CO_2 was quit low (TOF, 0.04 h^{-1}) and 2.5 times larger amount of H_2 was also produced from sacrificial agent. It was claimed that the low CO productivity in the heterogeneous system was caused by the decrease in the electron transfer from the Ru complex on the polymer surface to the Co complex in the solution. Ramaraj et al. investigated metal phthalocyanines adsorbed onto a Nafion membrane, which behaved as a p-type photocatalyst, for photoreduction of CO_2 in acidic aqueous solution containing TEOA as a hole scavenger [38,39]. HCOOH, another two electron reduction product, was mainly produced with a TOF of 3.0 h^{-1} with ZnPC/Nf (zinc phthalocyanine adsorbed on Nafion membrane). Recently, Motohiro et al. synthesized a hybrid photocatalyst consisting of a ruthenium complex and p-type photoactive N-doped Ta_2O_5 by a direct assembly method and used for the reduction of CO_2 in MeCN/TEOA under visible light irradiation [40,41]. The electron transfer from Ta_2O_5 to Ru complex leads to the two electron reduction of CO_2 to HCOOH. However, when metal complexes are fixed to a solid matrix, dissociation of ligands from a metal ion could be suppressed due to restricted mobility. The development of more efficient heterogeneous catalysts including anchored metal complex catalysts is desirable for the efficient multielectron photoreduction of CO_2.

In the present work, the authors designed novel heterogeneous CO_2-philic Pd complex catalysts (Pd-F/F-SiO_2) through immobilizing fluorinated Pd complexes onto the surface of silica support functionalized with long fluorinated hydrocarbon chains. Palladium catalyst, rather than the commonly Re and Ru, was selected because it is more selective to hydrocarbon species for the reduction of CO_2 [42,43]. The

recombination of H atom is retarded on the Pd surface decreasing the production of H_2 from hydrogen donor such as TEA [44,45]. The present Pd-F/F-SiO_2 shows a much higher rate of CO production of 14.8 h^{-1} when the photoreduction of CO_2 was carried out in DMF/TEA solution under ambient CO_2 pressure (entry 5). It was assumed the anchored Pd complex was more efficient and suitable for the photoreduction of CO_2 due to its unique properties: 1) good light harvesting as evidenced by UV-Vis measurement of Fig. 2, 2) good mobility and action of the CO_2-philic Pd complex in the CO_2-dissolved liquid phase, 3) good stability and durability of the anchored Pd complex for which interactions with F-SiO_2 suppress its leaching and decomposition, 4) easy desorption of the byproduct of H_2O to the solution promoting the reaction.

Table 4

4. Conclusions

The selective photoreduction of CO_2 to CO can be achieved in CO_2-dissolved expanded DMF solvent with TEA as an electron donor and novel heterogeneous CO_2-philic Pd complex catalysts. The catalysts used are fluorinated Pd complexes anchored onto a silica support modified by long fluorinated hydrocarbon chains. A high TOF of 65 h^{-1} and the 100% selectivity to CO were obtained with the most active catalyst at a temperature of 323 K and at a CO_2 pressure of 4 MPa. This excellent performance, compared to the literature data, may result from an effective combination of the CO_2-dissolved DMF and the CO_2-philic Pd catalyst. In this multiphase catalytic reaction system designed, the CO_2 concentration in DMF can be enhanced, the anchored fluorinated Pd complex can work well in the CO_2-philic medium, and the Pd complex

catalyst can be well stabilized, which prevents the immobilized active Pd species from leaching and decomposing to inactive metallic Pd species. It is further suggested that the light harvesting can be enhanced and the light of a wider range of wavenumber can be used with the anchored Pd complexes compared to the unsupported free complexes.

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Tables and Figures:

Table 1

Results of photocatalytic reduction of CO_2 in four different reaction systems

Entry	Solvent	CO_2 pressure (MPa)	System[a]	TOF (h^{-1})			Selectivity (%)	
				CO	CH_4	H_2	CO	CH_4
1	DMF	0.1	a	14.8	nd	3.2	100.0	0
2	CO_2	4	b	41.7	5	8.8	89.4	10.6
3	CO_2-DMF	4	c	65.8	nd	0.5	100.0	0
4	CO_2-DMF	8	d	11.0	nd	nd	100.0	0

Reaction conditions: 2 wt% Pd-F_{23}/F-SiO_2 20 mg, DMF 10 cm^3, TEA 2 cm^3, 323 K, 18 h. nd: not detected. TOF: turnover frequency = (moles of product formed)/((moles of Pd complex used)(reaction time)). [a] shown in Figure 3.

Table 2

Results of photoreduction of CO_2 in CO_2 expanded different organic solvents

Entry	Solvent	$E_T(30)$ (kcal mol^{-1})	TOF (h^{-1})			Selectivity (%)	
			CO	CH_4	H_2	CO	CH_4
1	DMF	30.6	65.8	nd	0.5	100	0
2	NMP	28.2	29.0	10.8	1.0	72.9	27.1
3	THF	16.4	24.2	8.8	1.4	73.3	26.7
4	MeCN	36.5	6.3	12.6	2.1	33.3	66.7

Reaction conditions: 2 wt% Pd-F_{23}/F-SiO_2 20 mg, CO_2 4 MPa, solvent 10 cm^3, TEA 2 cm^3, 323 K, 18 h. nd: not detected. TOF: turnover frequency = (moles of product formed) / ((moles of Pd complex used)(reaction time))

Table 3

Results of photoreduction of CO_2 with different Pd complex in CXLs

Entry	Catalyst	Amount of catalyst	TOF (h^{-1})	
			CO	H_2
Heterogeneous				
1	2 wt% Pd-F_{23}/F-SiO_2	20 mg	65.8	0.5
2	2 wt%Pd-F_{21}/F-SiO_2	20 mg	21.7	0.7
3	10 wt%Pd-F_{23}/F-SiO_2	20 mg	44.9	1.0
4	10 wt%Pd-F_{21}/F-SiO_2	20 mg	19.2	1.5
5	10 wt%Pd-F_{23} + F-SiO_2	20 mg	35.1	0.4
6	10 wt%Pd-F_{21} + F-SiO_2	20 mg	14.5	0.3
Homogeneous				
7	Pd-F_{23}	1.5 μmol	9.6	0.3
8	Pd-F_{21}	1.5 μmol	11.5	0.1

Reaction conditions: CO_2 4 MPa, DMF10 cm^3, TEA 2 cm^3, 323 K, 18 h. TOF: turnover frequency = (moles of product formed)/((moles of Pd complex used)(reaction time)).

Table 4 Comparison of the present heterogeneous Pd complex with other anchored metal complex in the literature for photoreduction of CO_2 under ambient CO_2 pressure

Entry	Catalyst	Temperature	Solvent	Product	TOF (h^{-1})	Ref.
1	[a]Re/Bp-PMO	293 K	MeCN	CO	0.1	[32]
2	[b]Ru-Co/Nf	Room temp.	DMF+H_2O	CO	0.04	[33]
3	[c]ZnPC/Nf	Room temp.	H_2O	HCOOH	3.00	[34,35]
4	[d]Ru/N-Ta_2O_5	Room temp.	MeCN	HCOOH	2.0	[36,37]
5	[e]PdF/F-SiO_2	323 K	DMF	CO	14.8	Present work

[a] Re/Bp-PMO: mesoporous biphenyl-silica (Bp-PMO) anchored fac-[Re(bpy)$(CO)_3(PPh_3)$]CF_3SO_3, 300 W Xe lamp equipped with a mirror module and a band-pass filter (280 or 365 nm, half-width of 10 nm), sacrificial agent TEOA.

[b] Ru-Co/Nf: a partially heterogeneous system, $[Ru(bpy)_3]^{2+}$ as a photosensitizer was fixed to cation exchange Nafion while $[Co(bpy)_3]^{2+}$ was used a homogeneous catalyst. 500 W Xe lamp with an IR-cut filter, sacrificial agent TEOA.

[c] ZnPC/Nf: Zinc phthalocyanine (ZnPC) adsorbed Nafion membrane, 500 W W-Hg lamp with a water filter and a Pyrex-glass filter to cut off IR and UV radiation, sacrificial agent TEOA.

[d] Ru/N-Ta_2O_5: $[Ru(dcbpy)_2(CO)_2]^{2+}$ anchored on p-type N-doped Ta_2O_5 functionalized with an PO_3H_2. 500 W Xe lamp with filter to produce light in the range $410 \leq \lambda \leq 750$ nm. sacrificial agent TEOA.

[e] PdF/F-SiO_2: 2 wt% Pd-F_{23}/F-SiO_2, sacrificial agent TEA.

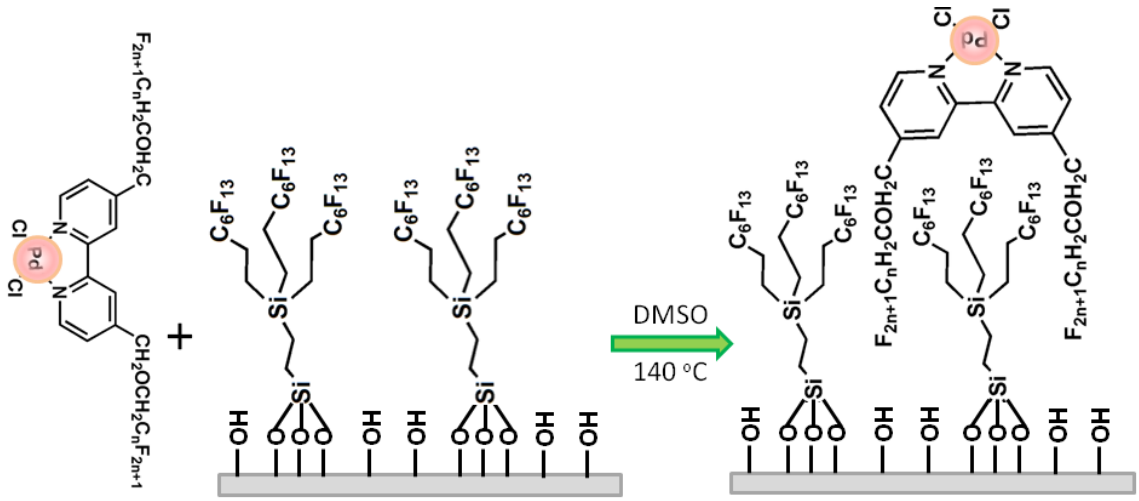

Fig. 1. Synthesis of CO_2-philic photocatalysts through anchoring of fluorinated Pd complexes onto the fluorinated silica.

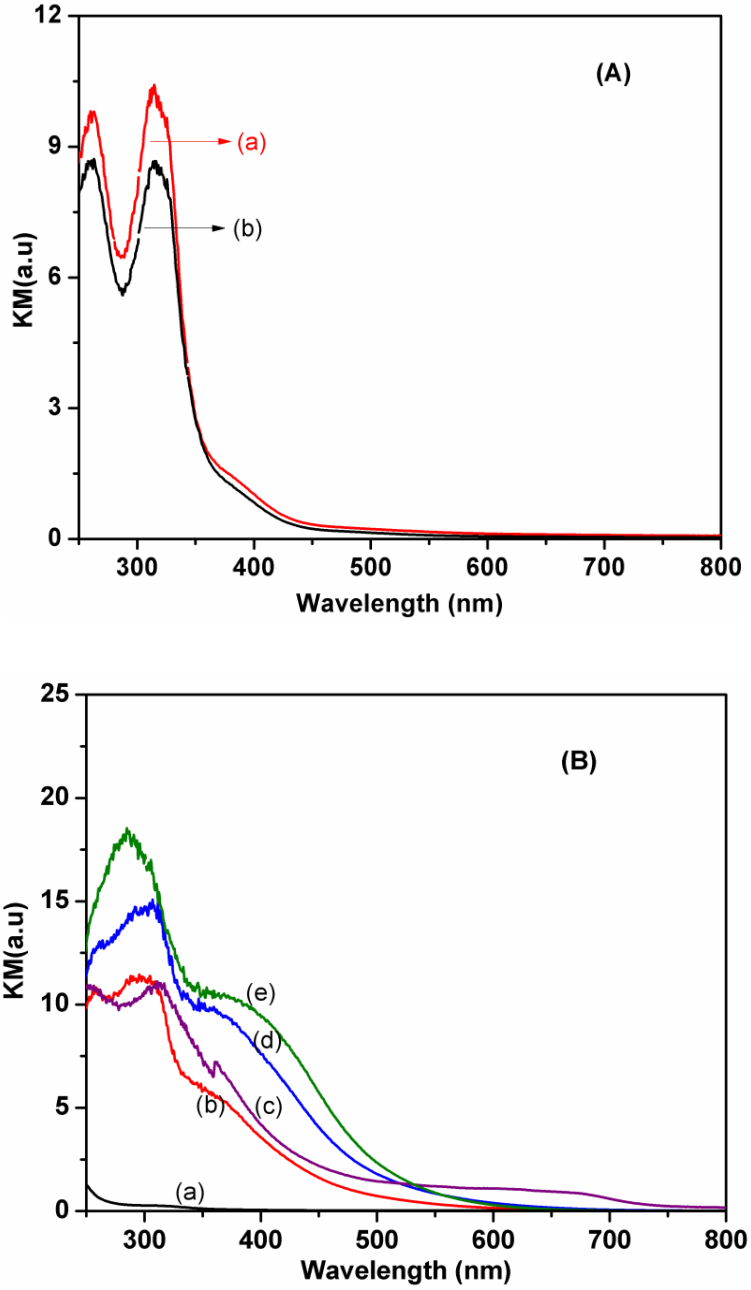

Fig. 2. Diffuse reflectance UV–Vis spectra of (A) unsupported Pd complexes (a) Pd-F_{21}, (b) Pd-F_{23}; (B) F-SiO_2 supported Pd complexes (a) F-SiO_2, (b) 2 wt% Pd-F_{21}/F-SiO_2, (c) 10 wt% Pd-F_{21}/F-SiO_2, (d) 2 wt%Pd-F_{23}/F-SiO_2, and (e) 10 wt% Pd-F_{23}/F-SiO_2.

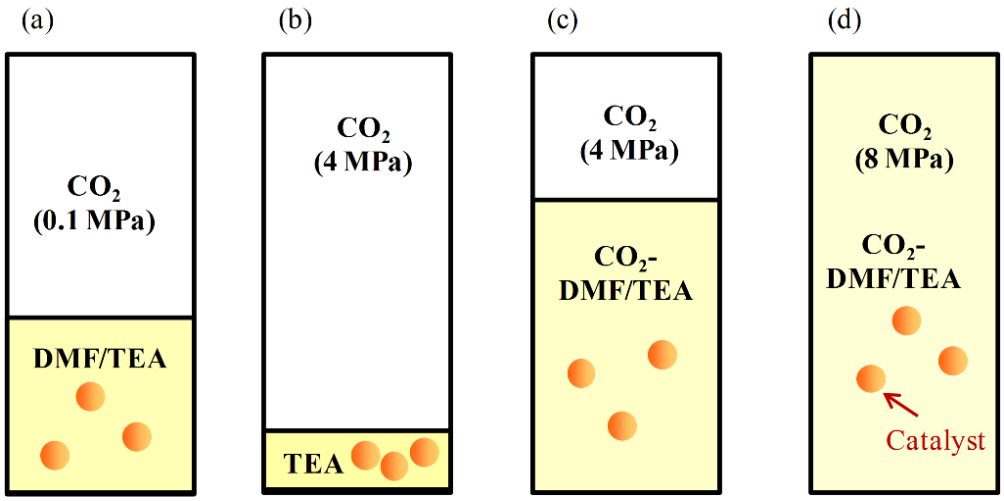

Fig. 3. Phase behavior of different reaction systems for photoreduction of CO_2.

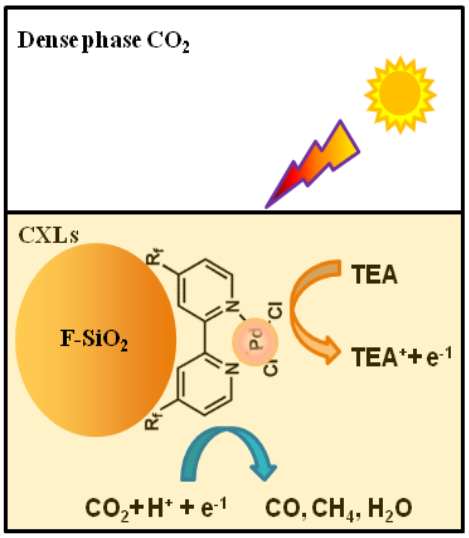

Fig. 4. Photoreduction of CO_2 with the CO_2-philic heterogeneous Pd complex anchored on fluorinated silica using TEA as electron donor in a CO_2-dissolved liquid phase.

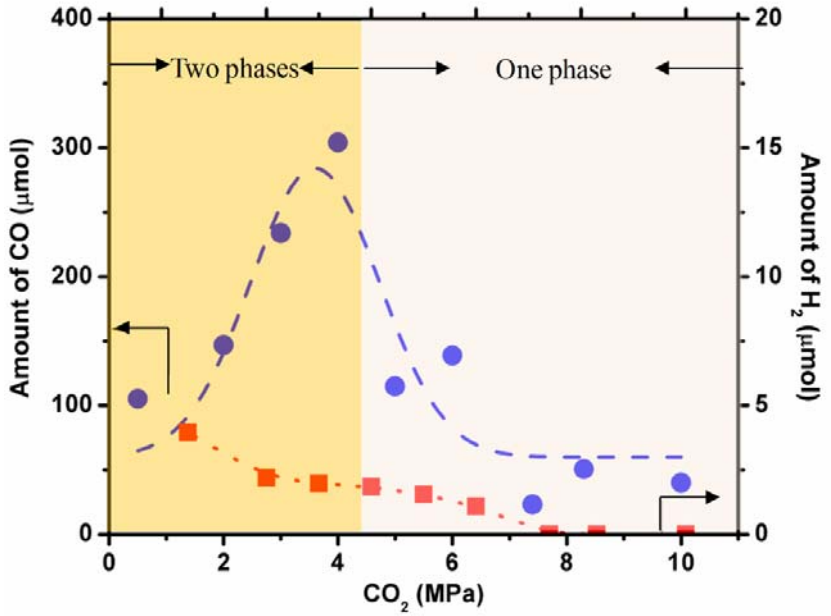

Fig. 5. Effect of CO_2 pressure on the photoreduction of CO_2 with 2 wt% Pd-F_{23}/F-SiO_2 in CO_2-expanded DMF. Reaction conditions: 2 wt% Pd-F_{23}/F-SiO_2 20 mg, DMF 10 cm^3, TEA 2 cm^3, 323 K, 18 h.

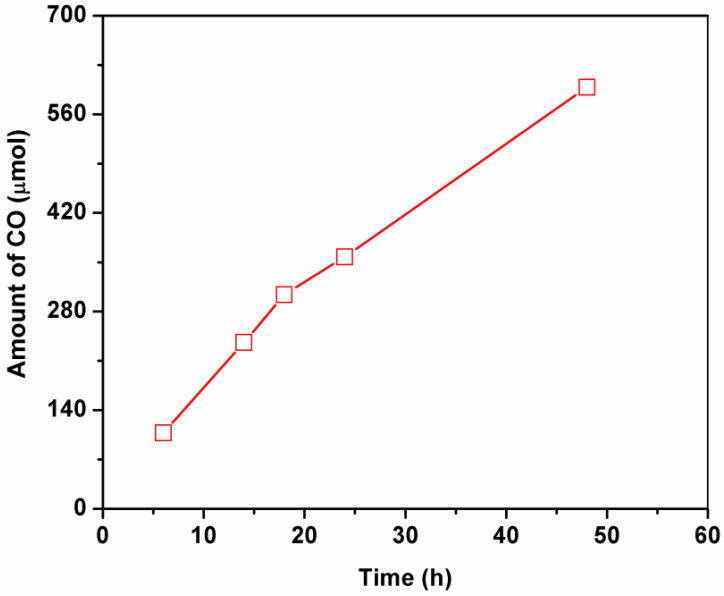

Fig. 6. Time profile of photoreduction of CO_2 with 2 wt% Pd-F_{23}/F-SiO_2 in CO_2-expanded DMF. Reaction conditions: 2 wt% Pd-F_{23}/F-SiO_2 20 mg, CO_2 4 MPa, DMF 10 ml, TEA 2 ml, 323 K.