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Authors: Zhimin Liu, Huan Wang, Yanfei Zhao, Yunyan Wu, Ruipeng Li, Hongye Zhang, Bo Yu, Fengtao Zhang, Junfeng Xiang, and Zhenpeng Wang

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Hydrogenation of Carbon Dioxide to C_2 - C_4 Hydrocarbons Catalyzed by Pd(P^tBu₃)₂-FeCl₂ with Ionic Liquid as a Cocatalyst

Huan Wang,^{[a, b], ‡} Yanfei Zhao,^{[a], ‡} Yunyan Wu,^[a, b] Ruipeng Li,^[a, b] Hongye Zhang,^[a] Bo Yu,^[a] Fengtao Zhang, ^[a, b] Junfeng Xiang, ^[a] Zhenpeng Wang^[a] and Zhimin Liu^{*[a,b,c]}

Abstract: Direct hydrogenation of CO₂ to C₂₊ hydrocarbons is very interesting, but achieving this transformation below 200 °C is challenging and seldom reported. Herein, we report a homogeneous catalytic system composed of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]), Pd(P'Bu₃)₂, FeCl₂ and ligand 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) for hydrogenation of CO₂ under mild conditions, which can realize the CO₂ hydrogenation to C₂-C₄ hydrocarbons in selectivity up to 98.3 C-mol% at 180 °C. The combination of [BMIm][PF₆] with Xantphos endows the Pd-Fe catalysts to be capable of activating CO₂ and H₂ simultaneously via forming [HPd(P'Bu₃)(BMIm-COO)(BMIm)(PF₆)Fe]⁺ species, thus catalyzing the formation of C₂-C₄ hydrocarbons from CO₂ hydrogenation. In addition, this catalytic system is stable and recyclable, which may have promising applications.

Carbon dioxide (CO₂) is a nontoxic, abundant, easily available, and renewable C1 resource, ^[1] and its hydrogenation into fuels and chemicals is of great significance for the sustainable development. C₂-C₄ hydrocarbons are the crucial chemical feedstocks for synthesizing value-added products such as detergents, polymer materials and drugs.^[2] The selective hydrogenation of CO_2 to C_2 - C_4 hydrocarbons is a promising way, but it imposes major technological challenges due to thermodynamic stability and kinetic inertness of CO₂ and suffers from low selectivity towards to C₂-C₄ hydrocarbons.^[3] So far, some heterogeneous catalysts have been developed for hydrogenation of CO_2 to C_2 - C_4 hydrocarbons.^[4] For instance, iron catalysts combined with K, Na, Ru, Zr promoters could realize this kind of transformation through reverse water gas reaction (RWGS) and Fischer-Tropsch synthesis (FTS) at 300-400 °C. [4b, 4d-f] Co-Fe bimetallic catalysts could catalyze the reaction at lower temperature (e.g. 270 °C), achieving C2+ hydrocarbons selectivity up to 69%.[4a] In most cases, the CO2 hydrogenation to C_2-C_4 hydrocarbons was performed at temperature higher than 250 °C, and that at temperature lower than 200 °C was seldom reported.^[5] To date, there is no report

on the CO₂ hydrogenation to C₂–C₄ hydrocarbons over homogeneous catalysts in a literature survey. The hydrogenation of carbon monoxide (CO) to light hydrocarbons has been widely investigated using homogeneous and heterogeneous catalysts.^[6] Ir₄(CO)₁₂ was reported to be capable of catalyzing the hydrogenation CO into methane (CH₄), ethane and trace amounts of propane and isobutene in molten NaCl-2AlCl₃ mixture, and AlCl₃ was found to promote the carbon chain growth through catalyzing the formation of CH₃Cl and CH₃CH₂Cl intermediates.^[6b-c]

lonic liquids (ILs) are a kind of salts composed totally of organic cations and inorganic/organic anions with high thermal and chemical stability, extremely low vapor pressure, nonflammability and tunable properties.^[7] Their unique features allow them to be widely applied in many fields, especially in CO₂ transformation as effective media.^[8] For example, imidazolium-based ILs combined with Ru catalysts realized the CO₂ hydrogenation to formic acid,^[8a] CO,^[8b] and CH₄,^[8c] respectively. The ILs generally played multiple roles in the reaction process with activating CO₂, stabilizing intermediates, and/or mediating the activity of the metal catalysts. Though much progress has been made, the IL-mediated CO₂ hydrogenation to hydrocarbons has been reported rarely in a literature survey.^[5, 8c]



Scheme 1. Synthesis of hydrocarbons from CO₂ hydrogenation.

Herein, we report the IL-promoted CO₂ hydrogenation to C₂-C₄ hydrocarbons over Pd(PtBu₃)₂-FeCl₂ homogeneous catalysts in the presence of ligand, 4,5-bis(diphenylphosphino)-9,9-dimethy-Ixanthene (Xantphos) at relatively low temperature (Scheme 1). In this protocol, the combination of 1-butyl-3-metylimidazolium hexafluorophosphate ([BMIm][PF₆]) with Xantphos modified the electronic states of Pd and Fe catalysts via forming active species including [HPd(Xanphos)]⁺, [Pd(Xanphos)(BMIm-COO)]⁺, [Pd(Xanphos)Cl]⁺ and [HPd(P^tBu₃)(BMIm-COO)(BMIm)(PF₆)Fe]⁺), which realized the activation of CO₂ and H₂ simultaneously, thus accomplishing the CO_2 hydrogenation to C_2 - C_4 hydrocarbons (including ethane, propane and n-butane) at 180 °C. With a gas mixture ($H_2/CO_2 = 2/1$) at 9 MPa, a yield of 1.08 C-mmol was achieved, together with the selectivity towards C₂-C₄ hydrocarbons up to 98.3 C-mol%, much higher than those obtained over the catalysts reported in literature.^[4] In addition,

[[]a] H. Wang, Dr. Y. Zhao, Y. Wu, R. Li, Dr. H. Zhang, Dr. B. Yu, F. Zhang, Dr. J. Xiang, Dr. Z. Wang and Prof. Dr. Z. Liu Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China E-mail: liuzm@iccas.ac.cn

[[]b] H. Wang, Y. Wu, R. Li, F. Zhang and Prof. Dr. Z. Liu

University of Chinese Academy of Sciences, Beijing 100049, China. [c] Physical Science Laboratory, Huairou National Comprehensive Science Center

 ^{[&}lt;sup>4</sup>] These authors contributed equally to this work. Supporting information for this article is given via a link at the end of the document.

the catalytic system was stable and reusable.

Various ILs and solvents were examined in the hydrogenation of CO₂ catalyzed by Pd(P^tBu₃)₂ and FeCl₂ in the presence of Xantphos ligand, and the results are listed in Table 1 and Table S1. It is clear that the ILs significantly influenced the reaction. [BMIm][PF₆], [EMIm][PF₆] and [BMIm][CI] were effective for CO₂ hydrogenation, and [BMIm][PF₆] afforded C₂-C₄ hydrocarbons (including ethane, propane and n-butane) as the main products with the selectivity up to 98.3 C-mol%, while [BMIm][CI] offered methanol as the main product accompanied with CH₄ (Table 1, entries 1-3, figures S1-S3). The differences in selectivity observed between the [BMIm][CI]- and [BMIm][PF6]-based systems may be ascribed to the differences in their interactions with water. The hydrophobicity of [BMIm][PF₆] can render the water formed in the reduction of CO₂ to be expelled from the catalytic active sites, which may be favorable to the C-C coupling to form C₂₊ products.^[5] While for hydrophilic [BMIm][CI], the formed water dissolves in the reaction system, which may influence the reduction of CO₂, preferentially forming methanol. [BMIm][NTf₂] was ineffective for the CO₂ hydrogenation without product detectable (Table 1, entry 4). For comparison, a weak Lewis base solvent, 1.3-dimethyl-2-imidazolidinone (DMI) that was used in CO₂ hydrogenation to acetic acid, higher alcohols and other hydrocarbons, [8d,9] were tested under the similar cond-

Table 1. The hydrogenation of CO_2 to hydrocarbons over different catalytic systems.^{[a]}

| Entry | IL | Product selectivity (C-mol%) | | | | Yield ^[I] (C-mmol) |
|-------------------|---------------------------|---------------------------------|-----------------|---------------|------|----------------------------------|
| | | CO | CH ₄ | C_2 - C_4 | MeOH | |
| 1 | [BMIm][PF ₆] | 0.7 | 1 | 98.3 | 0 | 1.08 |
| 2 | [EMIm][PF ₆] | 4.94 | 5.6 | 90 | 0 | 0.09 |
| 3 | [BMIm][CI] | 0 | 23 | 0 | 77 | 0.28 |
| 4 | [BMIm][NTf ₂] | 0 | 0 | 0 | 0 | 0 |
| 5 ^[b] | DMI | 0 | 0 | 0 | 0 | 0 |
| 6 ^[c] | [BMIm][PF ₆] | 28 | 72 | 0 | 0 | 0.02 |
| 7 ^[d] | [BMIm][PF ₆] | 64 | 36 | 0 | 0 | 0.05 |
| 8 ^[e] | [BMIm][PF ₆] | 0 | 0 | 0 | 0 | 0 |
| 9 ^[f] | [BMIm][PF ₆] | 0 | 0 | 0 | 0 | 0 |
| 10 ^[g] | [BMIm][PF ₆] | 57 | 43 | 0 | 0 | 0.04 |
| 11 ^[h] | [BMIm][PF ₆] | 0 | 0 | 0 | 0 | 0 |
| 12 ^[i] | [BMIm][PF ₆] | 0 | 0 | 0 | 0 | 0 |
| 13 ^[j] | [BMIm][PF ₆] | - | 39.1 | 60.9 | 0 | 0.11 |
| 14 ^[k] | [BMIm][PF ₆] | 0 | - | 0 | 0 | 0 |

[a] Reaction conditions: Pd(PⁱBu₃)₂ (40 µmol), FeCl₂ (40 µmol), Xantphos (80 µmol), IL (0.5 mL), CO₂ (3 MPa) and total (9 MPa) at room temperature, 180 °C, 12h. [b] DMI (0.5 mL). [c] Without Xantphos. [d] Without FeCl₂. [e] Without Pd(PⁱBu₃)₂. [f] Without Pd(PⁱBu₃)₂ and Xantphos. [g] Without FeCl₂ and Xantphos. [h] Only H₂ (9 MPa) was used as the reactant. [i] Only N₂ (3 MPa) was used. [j] CO (3 MPa) and total (9 MPa). [k] CH₄ (3 MPa) and total (9 MPa). [I] Yield denotes the total.

itions. However, no product was obtained (Table 1, entry 5), indicating that DMI inhibited the catalytic activity of Pd-Fe catalyst in this reaction system. Though [EMIm][PF₆] was effective for the CO₂ hydrogenation, the yield and the selectivity of C₂-C₄ hydrocarbons were much lower than those achieved in [BMIm][PF₆]. The above results indicated that the cooperation of cation and anion of the IL was responsible for their activity to promote the CO₂ hydrogenation to C₂-C₄ hydrocarbons.

To explore the roles of other components in the CO₂ hydrogenation, several control experiments were performed, and the results were listed in Table 1 (Entries 6-10). It was indicated that all Pd(P^tBu₃)₂, FeCl₂, Xantphos ligand and [BMIm][PF₆] were necessary for the production of C2-C4 hydrocarbons from CO₂ hydrogenation. Without Xantphos ligand or FeCl₂, the CO₂ hydrogenation in IL produced CO and CH₄ with small productivity, while the reaction did not occur in the absence of Pd catalyst. For comparison, Pd/C or other bidentate phosphine ligands including dppp (1.3-bis(diphenyphosphino)propane) and dppb (1,4-bis(diphenylphosphino)butane) were examined as well, however, only trace amount of CO were detected (Table S2, entries 1-3). From the above results, it can be deduced that each component of the designed catalytic system played vital roles in the formation of C2-C4 hydrocarbons. Furthermore, the catalytic system was treated with H₂ or N₂ without CO₂ under the similar conditions, respectively, and no products were detected in both cases (Table 1, entries 11 and 12), which excluded the possibility of the C₂-C₄ hydrocarbons originated from the organic components of the catalytic system. Thermogravimetric analysis (TGA) results indicated that [BMIm][PF₆] was stable in air up to 390 °C (Figure S4). ¹⁹F and ³¹P NMR of catalytic system before and after reaction also indicated that [PF₆]⁻ was stable under the experimental conditions (Figure S5). In addition, five catalytic cycles of CO₂ hydrogenation were conducted under the same conditions, and the yield of C2-C4 hydrocarbons almost remained unchanged at the fifth cycle, indicating that the catalytic system was stable and recyclable (Figure S6). IR of the remaining catalytic solution indicated that no formates and oxalates were



Figure 1. (A) XPS spectra of Pd 3d: a) $Pd(P^{1}Bu_{3})_{2}$; b) Pd-L; c) Pd-L-Fe. (B) XPS spectra of Cl 2p. (C) XPS spectrum of Pd 3d: Pd-L-Fe-F. (D) Fe L-edge soft XANES spectra: e) FeCl₂; f) Fe-L; g) Pd-L-Fe; h) Pd-L-Fe-F.

produced in the reaction process (Figure S7).

From the above results, it is obvious that Pd(P^tBu₃)₂ was the main catalyst for the CO₂ hydrogenation, and other components including Xantphos, FeCl₂ and [BMIm][PF₆] were necessary for the production of C₂-C₄ hydrocarbons in high selectivity. In order to explore the influences of every component on the activity of Pd(PtBu₃)₂ in the reaction process, three samples made of Pd(P^tBu₃)₂ with Xantphos ligand (denoted as Pd-L), with Xantphos and FeCl₂ (denoted as Pd-L-Fe), and with Xantphos, FeCl₂ and [BMIm][PF₆] (denoted as Pd-L-Fe-F) were, respectively examined by means of X-ray photoelectron spectroscopy (XPS). In the Pd 3d spectrum of Pd(PtBu3)2 (Figure S8 a), two pairs of peaks with binding energies (BEs) at 335.24, 340.49 and 337.19, 342.38 eV, are assigned to Pd⁰ and Pd²⁺.^[10] Compared to that of Pd(PtBu₃)₂, the spectra of Pd-L, Pd-L-Fe and Pd-L-Fe-F changed accordingly, which indicate that all Xantphos, FeCl₂ and [BMIm][PF₆] can influence the electronic environment and coordination of Pd (Figure 1 A and C, figure S8 b-c). Figure 1A illustrates that the BEs of Pd⁰ and Pd²⁺ of Pd-L and Pd-L-Fe shifted to smaller values in sequence compared to those of Pd(P^tBu₃)₂, Furthermore, the P 2p (Figure S8 d-a) and CI 2p XPS spectra (Figure 1B) also revealed that the P atoms of Xantphos and PF6⁻ and Cl⁻ from FeCl₂ coordinated with the Pd and Fe atoms. The above results suggest that Pd(P^tBu₃)₂ was activated by Xantphos and Cl⁻, and thus apt to coordinate with the imidazole ring of [BMIm][PF₆], supported by the N1s XPS analysis (Figure S8 h and i). As illustrated in Figure 1C, the Pd 3d spectrum of Pd-L-Fe-F can be deconvoluted into three pairs of peaks, which are assigned to 3d_{5/2} and 3d_{3/2} signals for Pd⁰ (335.15 and 340.43 eV), Pd+(336.76 and 342.26 eV), and Pd²⁺(337.72 and 343.0 eV), respectively.^[10] Here, it is worthy pointing out that the Pd⁺ species appeared in Pd-L-Fe-F, which may result from the Pd- π coordination between imidazole ring and the Pd catalyst.^[11a] In addition, a signal of Pd_{5/2} was observed at 336.76 eV, which was corresponded to Pd-F bond (Figure 1C and Figure S8 j).^[11b] The XPS analysis indicates that the modification of Pd(PtBu₃)₂ with [BMIm][PF₆] and Xantphos altered the electronic state of Pd species, and Pd-L-Fe-F may show activity different from Pd(PtBu3)2.



Figure 2. HR-ESI-MS spectrum of the reaction solution. Reaction conditions: $Pd(P^tBu_3)_2$ (80 µmol), FeCl₂ (80 µmol), Xantphos (160 µmol), [BMIm][PF₆] (2 mmol), CO₂ (3 MPa) and total (9 MPa) at room temperature, 180 °C, 3h.

The Fe L-edge soft XANES spectra of FeCl₂ together with Fe-L (composed of FeCl₂ and Xantphos), Pd-L-Fe and Pd-L-Fe-F were collected, as shown in Figure 1D (e and f). The distinct splitting of L₃-edge with a small post-peak (~709.9eV) and a main peak (~707.9eV) indicated the presence of only Fe²⁺ form in FeCl₂,^[12] consistent with the results of Fe 2p XPS analysis (Figure S8, k).^[13] However, the L₃ edge of Fe-L-Pd (Figure 1D, g) shows two main peaks at 708.1 and 709.5 eV, revealing that Fe was in two different chemical environments. While, in the spectrum of Pd-L-Fe-F the intensity ratio between the second and the first peaks reached up to 66.7/33.3, which suggested the complexed chemical interactions among Fe, Pd, Xantphos and [BMIm][PF₆] (Figure1D, h).

To elucidate ionic species in the reaction process, the reaction solution was analyzed by means of ESI-MS. As shown in Figure 2 and Figure S9, Pd species including [HPd(Xanphos)]⁺, [Pd(Xanphos)(BMIm-COO)]⁺ and [Pd(Xanphos)Cl]+ were detected in the ESI-MS(+) spectrum, suggesting that under the experimental conditions Pd species were mainly in the forms of Pd⁰, Pd⁺, Pd²⁺ complexed with Xantphos, carbene species ([BMIm-COO]) and Cl⁻, although much larger amount of PF6⁻ than Cl⁻ was present in the catalytic system. This is consistent with the results of XPS analysis. Moreover, the Pd-Fe bimetal species. [HPd(P^tBu₃)(BMIm-COO)(BMIm)(PF₆)Fe¹⁺, were also detected. These results indicated that the in situ generated complex was mainly in the form of Pd⁰- and Fe²⁺-complexed with P^tBu₃, [BMIm-COO], [BMIm]⁺ and PF₆⁻, which could activate CO₂ and H₂ simultaneously^[14] and may be responsible for catalyzing the CO₂ hydrogenation to C₂-C₄ hydrocarbons at relatively low temperature (e.g., 180 °C). From the above findings, it can be deduced that the high activity of the catalytic system was attributed to the synergetic effect from the active metal species stabilized by [BMIm][PF6] combined with the Xantphos ligand.



Scheme 2. Proposed mechanism of the reaction over the Pd-Fe-ILs catalytic system.

To explore the possible reaction pathway of CO_2 hydrogenation to C_2 - C_4 hydrocarbons, the hydrogenation of CO and CH₄ were performed over the same catalytic system under the similar conditions, respectively. It was revealed that C_2 - C_4 hydrocarbons could be obtained from CO hydrogenation with low activity and selectivity, while no product was detected in the case of CH₄ (Table 1, entries 13 and 14). Consequently, it can be deduced that the formation of C_2 - C_4 hydrocarbons from CO₂ hydrogenation may be undergo the CO pathway. Moreover, the reaction solution of CO_2 hydrogenation in [BMIm][PF₆] was

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examined by GC-MS (Figure S10). Trace amounts of CH₃Cl and CH₃CH₂Cl were detected, which are possible intermediates to form CH₄, ethane, propane and n-butane.^[6c] Based on the experimental results and previous reports,[6c], [15] a possible reaction pathway is proposed as shown in Scheme 2. Firstly, CO is generated via Pd* catalyzed CO₂ hydrogenation (Step 1), ^[16] which is then coordinated with Pd* to form the Pd*CO complex (Step 2). The HPd*CHO complex may be formed via the hydrogenation of Pd*CO complex (Step 3), which further reacts with H₂ and Cl⁻ to convert into CH₃Pd*Cl promoted by Fe* (Step 4). Subsequently, CO inserts into the CH₃-Pd* bond, which easily occurs,^[17] generating CH₃COPd*Cl (Step 5). Followed by hydrogenation, CH₃CH₃ is formed (Step 6). The generation of propane and n-butane from CH₃CH₂CI maybe follow the similar steps. In this work, the Fe catalyst mainly promotes the formation of CH₃Cl and CH₃CH₂Cl intermediates,^[6c] while the Pd catalyst is responsible for hydrogenation (Table 1, entry 8). [BMIm][PF6] and ligand (Xantphos) play vital roles in modifying the electronic states of Pd and Fe catalysts and stabilizing the metal-based active species (Table 1, entries 1 and 3).

In summary, [BMIm][PF₆] could promote the selective hydrogenation of CO₂ over the Pd-Fe homogeneous catalysts, yielding C₂-C₄ hydrocarbons including ethane, propane and n-butane in selectivity up to 98.3 C-mol% and yield as high as 1.08 C-mmol at 180 °C. The catalytic system could be recycled and reused for at least 5 times without activity loss. The IL and Xantphos ligand complexed with Pd and Fe to form active species, which could activate CO₂ and H₂ simultaneously, further catalyzing the CO₂ hydrogenation to C₂-C₄ hydrocarbons. We believe that this kind of catalytic system may find promising applications in the transformation of CO₂ to C₂₊ alcohols/hydrocarbons under mild conditions. Further work is under way in our group.

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Keywords: ionic liquid • CO_2 hydrogenation • Pd–Fe homogeneous catalysis • C_2 - C_4 hydrocarbons synthesis

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Entry for the Table of Contents

Layout 1:

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The $[BMIm][PF_6]$ -based $Pd(P^tBu_3)_2$ -FeCl₂ homogeneous catalytic system can realize CO₂ hydrogenation to C₂-C₄ hydrocarbons under mild conditions (e.g., 180 °C).



Huan Wang,^{[a, b],+} Yanfei Zhao,^{[a],+} Yunyan Wu,^[a, b] Ruipeng Li,^[a, b] Hongye Zhang,^[a] Bo Yu,^[a] Fengtao Zhang,^[a, b] Junfeng Xiang,^[a]Zhenpeng Wang,^[a] and Zhimin Liu ^{[a, b],*}

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Hydrogenation of Carbon Dioxide to C2-

C₄ Hydrocarbons Catalyzed by

Pd(P^tBu₃)₂-FeCl₂ with Ionic Liquid as a

Cocatalyst