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Hydrogenation of CO_2 to formic acid catalyzed by heterogeneous Ru-PPh_3/Al_2O_3 catalysts

Wenjing Zhang, Shengping Wang*, Yujun Zhao, Xinbin Ma

Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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ABSTRACT

The highly efficient, heterogeneous Ru-PPh_3/Al_2O_3 catalysts with the different molar ratios of Ru and PPh_3 (1:3, 1:6, 1:9, 1:12, 1:15) were prepared and employed in hydrogenation of CO_2 to formic acid. It was demonstrated that the indispensable electron-donation ligand PPh_3 increased the catalytic activity of Ru-PPh_3/Al_2O_3 via providing electrons to the Ru center. Procedures of dihydrogen coordination and CO_2 insertion into the Ru—H bond proceeded easily in the presence of the optimal quantity of the electron donor PPh_3, the protonic additive KH_2PO_4 and the appropriate co-solvent. A favorable turnover frequency of up to 751 h^{-1} was obtained over Ru-PPh_3/Al_2O_3(1:9) with 0.63 wt% Ru loading using KH_2PO_4 and PPh_3 as additives in the mixed solution of ethanol, trimethylamine, and H_2O.

1. Introduction

Formic acid is considered to be one of irreplaceable raw materials in organic transformations [1]. Additionally, formic acid has been considered as a candidate for methanol-alternative fuels in methanol fuel cells, as the direct fuel for electricity generation, and as a fuel for automobiles due to its much better electrochemical oxidation [2]. Hydrogenation of carbon dioxide (CO_2), an efficient and environmentally friendly approach, has contributed to significant contemporary interest in formic acid production mediated by transition-metal compound [3]. The past several decades have witnessed an explosion in efforts directed towards the homogeneous catalytic CO_2 hydrogenation to formic acid with diverse organometallic complexes, a highly promising class of which is Ru complex. However, it creates difficulties major in separating and recovering catalysts for commercial scale synthesis of formic acid although amazing reactivity has been obtained in homogeneous catalysis. Compared to the homogeneous catalysts, the catalytic performance of the separable heterogeneous catalysts with good reusability is routinely dissatisfactory [4]. The electron-donation ligands around Ru which can provide electrons to the reaction system are responsible for the high catalytic activity of the homogeneous catalysts [5,6]. Hence, we were drawn to exploit a heterogeneous catalyst applied to the conversion of CO_2 to formic acid via hydrogenation, possessing appropriate electron-donation ligands around Ru as alternatives to precious organometallic catalysts.

As a fantastic electron-donor, triphenylphosphine (PPh_3) favors to coordinate with Ru center firmly [7,8]. It has attached considerable attention as one of the best feasible ligands of Ru in homogeneous catalytic hydrogenation of CO_2 to formic acid [9,10]. On the other hand, PPh_3 has been implicated as an excellent additive in heterogeneous catalytic CO_2 hydrogenation over Si–$(CH_2)_3$–$NH(CH_2)_3CH_3$–Ru [11].

This work focuses on the fabrication of novel heterogeneous Ru-PPh_3/Al_2O_3 catalysts to catalyze the synthesis of formic acid from hydrogenation of CO_2. A probe into the electron-donating or protonic additives of this reaction was also explored to reveal the positive effect of additives on the catalyzed CO_2 hydrogenation. A probable catalytic mechanism of CO_2 hydrogenation to formic acid over Ru-PPh_3/Al_2O_3 was proposed and presented, particularly with the assistance of PPh_3 in the reaction of formic acid production.

2. Experimental

2.1. Catalyst preparation

For a typical synthesis of Ru-PPh_3/Al_2O_3 (1:9), 0.100 g $RuCl_3 \cdot xH_2O$ (J&K Scientific Ltd.) was resolved in 10.0 mL absolute ethanol solution (Tianjin kwangfu Fine Chemical Industry Research Institute). And then 15.0 mL absolute ethanol solution of PPh_3 (Tianjin kwangfu Fine Chemical Industry Research Institute) and 5.00 g γ-Al_2O_3 with a specific surface area of 121 $m^2 \cdot g^{-1}$ (Tianjin kwangfu Fine Chemical Industry Research Institute) was added under strong magnetic stirring. The

* Corresponding author.
E-mail address: spwang@tju.edu.cn (S. Wang).

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solution was refluxed under N_2 atmosphere at 80 °C for 4 h. The obtained light red-brown solid of the complex was washed with ethanol followed by spin flash drying at 50 °C for 0.5 h and then dried at 80 °C overnight in vacuum. The five as-prepared catalysts with the different molar ratios of Ru and PPh_3 were named as Ru-PPh_3/Al_2O_3 (1:3), Ru-PPh_3/Al_2O_3 (1:6), Ru-PPh_3/Al_2O_3 (1:9), Ru-PPh_3/Al_2O_3 (1:12) and Ru-PPh_3/Al_2O_3 (1:15), respectively.

2.2. Hydrogenation of CO_2 to formic acid

The catalytic behavior of the materials was investigated in the hydrogenating of carbon dioxide to formic acid. Reactions were performed in a 100 mL stainless steel autoclave with a magnetic stirrer. In a typical operation, 3.2 g Ru-PPh_3/Al_2O_3 (1:9) catalyst with 0.63 wt% Ru loading (according to the result of ICP), 30.0 mL of absolute ethanol and 10.0 mL of triethylamine (NEt_3) were added to the autoclave. After flushing the reactor three times with H_2, CO_2 was pumped to 6.0 MPa from a steel cylinder equipped with a siphon, then the reactor was pressurized by H_2 to 12.0 MPa at the required temperature. The autoclave was heated by a mantle equipped with a temperature controller to 80 °C. At the same time, the pressure reached about 14.5 MPa which was regarded as the start of the reaction. After reacting for one hour, the autoclave was cooled to the room temperature. The liquid in the reactor was analyzed by an Agilent High Performance Liquid Chromatography (Tape 1100) equipped with prevail organic acid column (Grace from America, 250 mm × 4.6 mm) and a variable wavelength scanning UV detector. Turnover frequency (TOF) is used to express the yield of formic acid, which reflects the moles of formic acid produced per mole of ruthenium per hour. TOF was calculated based on the actual Ru amount of the catalyst.

2.3. Catalyst characterization

2.3.1. Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectroscopic measurements were conducted on a Thermo Scientific Nicolet 6700 equipped with a deuterated triglycine sulfate detector (DTGS) detector. The powder of catalysts was pressed into a KBr-diluted self-supporting wafer and then scanned from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Moreover, a determination was operated by making samples with the roughly same quantity of catalysts and potassium bromide to make the results more comparable.

2.3.2. Powder X-ray diffraction

Powder X-ray diffraction (XRD) crystalline phases were recorded on a Rigaku C/max-2500 diffractometer equipped with a Cu Kα radiation anode (λ = 1.54056 Å, 40 kV and 200 mA) at room temperature. The intensity of the signal was measured by step scanning over 2θ range from 10 to 90° with a scanning rate of 5°min^{-1}.

2.3.3. Inductively coupled plasma-optic emission spectroscopy

The actual Ru amount of the catalyst was measured by Inductively Coupled Plasma-Optic Emission Spectroscopy (ICP-OES) (Varian Inc., VISTA-MPX). Argon was taken as the carrier gas and created the plasma. 10 mg of the sample was digested in 3 mL sulfuric acid, 3 mL phosphoric acid and 2 mL deionized through an 800 W microwave oven (Anton Parr, Multiwave 3000) for 1 h.

2.3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted with a Perkin-Elmer PHI 1600 ESCA system equipped with Al Kα (1486.6 eV) radiation as the excitation source under ultrahigh vacuum (1.33×10^{-8} Pa). The samples were fixed to the specimen holder with double-sided adhesive tape. Calibration of the binding energy was accomplished with respect to the internal standard of the signature C1s peak for adventitious carbon at 284.6 eV to determine the charging effect. Fitting of the peaks was made by using the software XPS PEAK41.

2.3.5. Transmission electron microscope

Transmission electron microscope (TEM) analysis was operated on a JEOL JEM-2100F, the point and linear resolution of which are 0.19 and 0.1 nm, respectively. A bit amount of the as-prepared Ru-PPh_3/Al_2O_3 catalyst was grounded before being dispersed in ethanol and spread onto copper grids.

3. Results and discussion

3.1. Performance of Ru-PPh_3/Al_2O_3 catalysts

3.1.1. Effect of PPh_3 as electron-donation ligand in the catalyst preparation

As for tertiary phosphine complexes of ruthenium, a facile dissociation in solution was reported by T. A. Stephenson and G. Wilkinson [12]:

$$[RuCl_2(PPh_3)_4] + \text{solvent} \leftrightarrow [RuCl_2(PPh_3)_2(\text{solvent})_2] + 2PPh_3$$

Indeed, the configurations of these mononuclear complexes of Ru tremendously depend upon the adding amount of ligands. To explore the ideal molar ratio of PPh_3 and Ru for Ru-PPh_3/Al_2O_3, a series of catalysts were synthesized and applied to CO_2 hydrogenation. As labeled in Fig. 1, the conversion of CO_2 increased immensely until the molar ratio of PPh_3 and Ru was 9:1, which was the optimum molar ratio for Ru-PPh_3/Al_2O_3. The Ru-PPh_3/Al_2O_3 (1:9) catalyst gave a TOF of 263 h^{-1}. It is also noted that a homogeneous Ru-PPh_3 catalyst gave a TOF of 39 h^{-1} and Al_2O_3 was not active for the synthesis of formic acid under the same condition. In the absence of PPh_3, chlorine or the solvent ethanol tends to coordinate with Ru. However, neither chlorine nor ethanol is qualified to be a superior electron-donation ligand as PPh_3. That is, chlorine and ethanol couldn't provide electrons to Ru and promote the catalysis any further. While, extra PPh_3 induced an unnecessary combination with the carrier instead of Ru, which led to an increase of steric hindrance, further hindering the elimination of formic acid from the catalysts [13].

Thus, Ru-PPh_3/Al_2O_3 (1:9) impregnated with a 1:9 of Ru:PPh_3 molar ratio at 80 °C for 4 h, was employed as the effective catalyst for CO_2 hydrogenation in the following experiments unless stated otherwise.

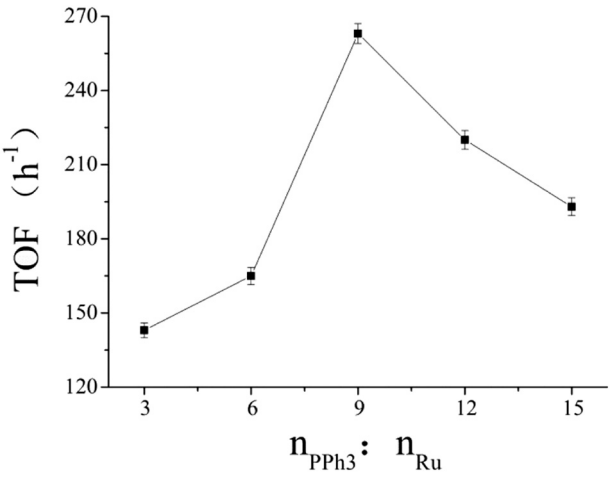

Fig. 1. Effect of the amount of PPh_3 in Ru-PPh_3/Al_2O_3 on the production of formic acid.
Reaction conditions: 0.2 mmol Ru-PPh_3/Al_2O_3, 10.0 mL NEt_3, 30.0 mL CH_3CH_2OH, 80 °C, 1 h.