



Catalytic reduction of carbon dioxide by nickel-based catalyst under atmospheric pressure

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HIGHLIGHTS

- Ni–P/Al₂O₃ proved to be effective for catalyzing CO₂ reduction.
- A new method of CO₂ resource utilization under atmospheric pressure was developed.
- The reaction mechanism was proposed according to the characterizations of products.

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ABSTRACT

To develop a new method of CO₂ resource utilization, the screening tests of catalysts were carried out, and Ni–P/Al₂O₃ was established as the most suitable composite catalyst for CO₂ catalytic reduction. By optimizing, the main preparation conditions of Ni–P/Al₂O₃ were obtained with Ni/P of 1:1, impregnation time of 12 h and calcination temperature of 550 °C. For CO₂ reduction based on Ni–P/Al₂O₃ catalysis, the optimal experimental conditions were determined as Ni–P/Al₂O₃ content of 1%, sodium borohydride (NaBH₄) concentration of 0.175 mol L⁻¹, reaction temperature of 55 °C, pH of 8.0, ethanol concentration of 90%, and residence time of 15 s. And 41.37% of the average efficiency of CO₂ reduction was reached. Compared with the results of non-catalytic conditions, the NaBH₄ dosage was reduced by 60.14%, which indicated the excellent catalytic ability of Ni–P/Al₂O₃ on CO₂ reduction, from which, the innovative method of the catalytic reduction of carbon dioxide (CO₂) by NaBH₄ under atmospheric pressure and moderate temperature was proposed. Based on the analyses of Scanning Electron Microscope, X-ray Powder Diffraction and Ion Chromatograph, the catalytic reduction mechanism of CO₂ by Ni–P/Al₂O₃ was revealed.

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1. Introduction

According to the data of International Climate Group-Carbon Monitoring for Action (CARMA), there are more than 60,000 coal-fired power plants in the world, and about 10 billion tons of carbon dioxide (CO₂) had been released into the atmosphere every year [1]. It should be noticed that once being released, CO₂ will be in the atmosphere for thousands of years, and a series of knock-on effects such as climate warming, sea level rise, hurricane aggravation, vegetation migrating, species extinction, etc. on climate change will be triggered.

In recent years, the investigations those CO₂ was reduced to useful chemicals or liquid fuels by catalytic or non-catalytic reactions have been reported [2–4]. In terms of the non-catalytic reac-

tion, CO₂ was converted into the chemical products of ammonia and urea, etc.; nevertheless, its application in power plants might be limited, due to the influences of the quantity and pressure of coal-fired flue gas [5]. Through the catalytic processes of CO₂ hydrogenation, CO₂ was reduced into carbon monoxide and methane by nickel (Ni) catalyst at 320–720 °C [6]. Under the conditions of 50 atm and 110 °C, the catalytic reduction that CO₂ was converted into formate (HCOO⁻) was studied by using the hydrogen donors such as isopropyl alcohol, cyclohexanol alcohol and benzene ethanol [7,8]. Obviously, some breakthroughs have been made for the current technologies of the catalytic conversion of CO₂, but the problems of high energy consumption and the complex operation conditions still remain to be solved. As a powerful reducing agent, the properties and applications of sodium borohydride (NaBH₄) have been investigated [9,10], among them, it was used to reduce CO₂ into boron-doped porous carbon at 500 °C and atmospheric pressure [11,12]. Although the reduction of CO₂

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into formic acid (HCOOH) by the hydrogen donor of NaBH₄ was studied at atmospheric pressure and lower temperature [13] recently, it had a disadvantage of the larger NaBH₄ dosage, resulting in the higher operating cost. For industrial application in the future, reducing the NaBH₄ dosage and the using amount of NaBH₄ and improving the reduction efficiency of CO₂ is very necessary. Hence, the catalytic reduction of CO₂ was investigated in this paper. A desired catalyst for CO₂ reduction was obtained by a comparison of the catalysts performance and the optimization of the preparation. At the same time, the optimal reaction conditions of CO₂ reduction were achieved by a series of influencing factor tests. On the basis of the characterizations of the catalysts and the products, the catalytic mechanism of CO₂ reaction with NaBH₄ was proposed.

2. Experimental

2.1. Materials

N₂ and CO₂ with the purity of >99.8% were purchased from North Special Gas Co., Ltd., China. The reagents (analytical grade) were obtained from Tianjin Chemical Reagents Company. All chemicals were used as received without further purification. Deionized water was produced by the lab water purification system (Changfeng Co., Ltd., Beijing), with the resistivity of >18.25 MΩ cm⁻¹.

2.2. Preparation of catalysts

In view of the reaction temperature in the range of 15–70 °C in the CO₂ reduction, the low-temperature activity of the catalyst should be considered in the preparation. Based on the previous studies [14–17], the active low-temperature catalysts of Ni and cobalt (Co) or their corresponding oxide metals had the excellent catalytic activity for CO₂ reduction. For comparison, the catalysts of Ni, cobalt (Co) and palladium (Pd) were prepared to investigate the CO₂ reduction.

A mixed solution containing cobalt chloride (CoCl₂, mass fraction of 20%), sodium phosphinate hydrate (NaH₂PO₄·H₂O, mass fraction of 3%) and deionized water was used to prepare Co catalyst by the reduction method [15], at room temperature. For the supported Ni catalysts preparation, the support powders such as TiO₂ [17], Al₂O₃ and TiO₂–Al₂O₃ which were prepared in advance were impregnated by the aqueous solutions of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and ammonium phosphate (NH₄H₂PO₄) [18], from which, Ni–P/TiO₂, Ni–P/Al₂O₃ and Ni–P/TiO₂–Al₂O₃ were obtained. The Pd/C catalysts were also prepared according to our previous work [19].

2.3. Experimental procedure

N₂ and CO₂ were metered through mass flow controllers (LZB, China) and mixed in a buffer bottle, in which CO₂ was diluted by N₂ to desired concentrations. At 0.1 MPa, the catalytic reduction of CO₂ was carried out in a bubble reactor (home-made) containing NaBH₄ and catalysts in ethanol and water. The reactions occurred when the mixed gas with the different gas flow rate (±1%) entered into the bubble reactor. The reaction temperature was adjusted from 15 °C to 70 °C by an electric-heated thermostatic water bath (HH-2, China). The solution pH was regulated by mixed acid and alkali buffer (phosphoric acid, acetic acid, boric acid and sodium hydroxide) and measured by a pH meter (PHSJ-5, China). Meanwhile, to evaluate the reducing capacity of the reaction system, the variations of CO₂ volume concentrations as a function of the reaction time were also examined. CO₂ concentration was detected

by an infrared gas analyzer (Xibi GXH510, China). According to the inlet and outlet CO₂ concentrations, the reduction efficiency of CO₂ was calculated by Eq. (1)

$$\eta_{ce} = (1 - \varphi_0/\varphi_i) \times 100\% \quad (1)$$

where η_{ce} : the reduction efficiency of CO₂, %; φ_i and φ_0 : the inlet and outlet CO₂ concentrations, respectively, %.

2.4. Characterizations

A high-resolution Scanning Electron Microscopy (SEM, JEOL JSM-7500F, USA) was used to investigate the microstructures of catalysts. An X-ray Powder Diffraction (XRD, Bruker D8 ADVANCE, Germany) was performed at a 2θ range of 10–70° and a step size of 0.02° to determine the active components of catalysts. An Ion Chromatograph (IC, Metrohm 792, Switzerland) was applied to characterize the reaction products.

3. Results and discussion

3.1. Screening of catalysts for CO₂ reduction

To select a suitable catalyst for CO₂ reduction and evaluate the reducing capacity of the reaction system NaBH₄, 5% and 10% of palladium/carbon [20] catalysts, Co catalyst and Ni catalyst were used in the catalyst screening experiments in which, the mass ratios of each catalyst to NaBH₄ were all 1.0%, and the reaction conditions such as gas flow rate, reaction temperature, solution pH and CO₂ concentration were fixed. The variations of CO₂ volume concentrations as a function of the reaction time were investigated, as shown in Fig. 1. Compared with the non-catalytic sample, Ni–P/TiO₂ catalyst had an obvious catalytic action for CO₂ reduction in the reaction time range of 0–1700 s. Nevertheless, other catalysts such as Co, 5% and 10% of palladium/carbon show the negative catalytic effect on CO₂ reduction. The reason might be that the roles of Co and Pd/C catalysts were mainly embodied in improving hydrogen release of NaBH₄ [16,20], which increased the decomposition of NaBH₄, resulting in the inhibition of the hydrogenation of CO₂ according to the previous work [17], it was easier for Ni species in Ni–P/TiO₂ catalyst to be reduced into the high activity Ni⁰ species which was beneficial to the activation of NaBH₄ and the hydrogenation of CO₂. In addition, it was also found from Fig. 1 that the

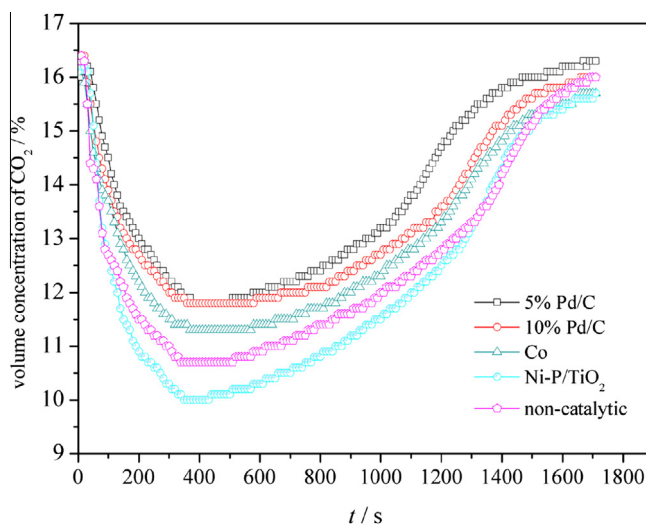


Fig. 1. Effects of different catalysts on CO₂ reduction. Ethanol concentration: 80%; NaBH₄ concentration: 0.175 mol L⁻¹; pH: 8.0; T: 45 °C; catalyst amount: 1.0%; residence time of gas: 15 s; absorption solution volume: 0.15 L.

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