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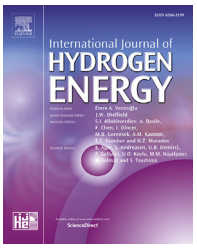

Hydrogenation of carbon dioxide under atmospheric pressure and low temperature

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ABSTRACT

In order to realize the effective reduction and utilization of carbon dioxide (CO_2) in coal-fired flue gas, a process was developed under atmospheric pressure that uses KBH_4 as an efficient hydrogen donor. By investigating the influencing factors of CO_2 conversion, the optimal experimental conditions were determined and the average CO_2 conversion efficiency of 50.36% was obtained when the KBH_4 concentration was 0.2 mol/L, reaction temperature was 50 °C, solution pH was 8, and flow rate was 300 mL/min. The experimental results also verified that the coexisting gases such as sulfur dioxide (SO_2), nitric oxide (NO) and oxygen (O_2) in flue gas had no significant competition or inhibition effect on CO_2 conversion. Meanwhile, the conversion products were analyzed by an Ion Chromatography (IC) and Fourier Transform Infrared Spectroscopy (FT-IR), and the results proved that the main reaction product was formate. Combined with the relevant literatures, the mechanism of CO_2 reaction with KBH_4 was proposed.

Introduction

The atmospheric concentration of carbon dioxide (CO_2) had been increased rapidly in the past decade because of the excessive utilization of fossil fuels [1,2]. The report on trends of global CO_2 emissions in 2015 showed that global CO_2 emission reached up to 35.7 billion tones in 2014 [3]. In that year, China and the United States increased their emissions by 0.9%. In the European Union, CO_2 emissions decreased by an unprecedented 5.4%, while India's emissions continued to increase strongly, by 7.8%. It is noteworthy that $CO_2$is the major greenhouse gas compared with methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorinated compounds (PFCs) and sulfur hexafluoride (SF_6), due to its greatest emissions.

For the carbon capture and resource utilization (CCRU) [4], physical and chemical solvents, various types of membranes, ionic liquids (ILs), nanoparticle organic hybrid materials, and chemical looping sorbents [5–7] have widely been investigated. Among of them, alkanol amine, ammonia solutions and ILs were the most commonly used for CO_2 absorbing [8–10]. However, in these processes exist energy-intensive and corrosion problems during the regeneration [11]. CO_2 absorption by ammonia solution may be an alternate approach, but it has the obvious disadvantage of ammonia escape from the absorption tower, causing secondary pollution and materials loss [11,12]. Scholars realize that CO_2 is a kind of industrial raw material, it can be reduced into chemical products and achieved the resource utilization [13–20]. Hence, organic and inorganic hydrogen reagents, such as isopropylalcohol [21], dimethylamine-borane [22], and ammonia-borane [23] have

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been used for CO_2 reduction. But the processes based on these hydrogen donors have the disadvantages of high-cost and high-energy consumption. As a consequence, the current methods of CO_2 hydrogenation using these hydrogen donors are difficult to carry out at an industrial scale.

We observe that as a kind of hydrogen donor, borohydride has been applied in the fields of direct fuel cells [24,25], fabrication of carbon nanotubes [26] and boron-doped porous carbon by using the CO_2 reduction [27,28]. Compared with $NaBH_4$, KBH_4 has the advantages of higher stability in water and lower price. Hence, the CO_2 reductions by KBH_4 in gas-liquid and gas-solid phases have been investigated [29,30]. For the existing researches in practical application in the future and to explore a feasible approach for the resource utilization of CO_2 at low cost, we examined the effects of various factors, such as KBH_4 concentration, reaction temperature, solution pH, gas flow rate and coexisting gases such as sulfur dioxide (SO_2), nitric oxide (NO) and oxygen (O_2) in flue gas on CO_2 reduction by KBH_4, under atmospheric pressure and moderate temperature, from which, the optimal experimental conditions were obtained. Meanwhile, the reaction mechanism was proposed based on the analyses of conversion products and the relevant literatures.

This process has the advantage of lower equipment investment, compared with processes that use H_2 or other hydrogen donors as reducing agents for CO_2 hydrogenation. Therefore, this work can provide a basis for the development of a technology with the potential of combining CO_2 emission reduction with CO_2 utilization at low cost.

Experimental

Materials

All gases in experiments were supplied by compressed gas steel cylinders (North Special Gas Co., Ltd., China), with the purity of >99.8%. All chemicals with analytical reagent (AR) were used without further purification (Tianjin Chemical Reagents Company). The high purity water that was applied to prepare the KBH_4solution was produced by the lab water purification system (Changfeng Co., Ltd., Beijing), with the specific resistance of >18.25 MΩ/cm.

For the preparation of reduction solution, a certain amounts of $KBH_4$was added into a beaker and diluted to desired concentration by water, and then the solution pH was adjusted from 6.0 to 10.0 by potassium hydroxide solution (1 mol/L) or hydrochloric acid solution (1 mol/L) to avoid the self-hydrolysis of KBH_4, like this, the KBH_4solution was obtained.

Experimental procedure

The experimental system composed of a bubble reactor (self-made) with 250 mL of effective volume and 15.5 cm of height, and a gas blanket of micron porous core fabric is located at 1.5 cm far from the bottom of reactor to evenly distribute gas flow, as shown in Fig. 1.

In the experiments, the metered N_2, CO_2, O_2, SO_2 and NO by mass flow controllers (LZB, Tianjin Flow Meter Co., Ltd., China)

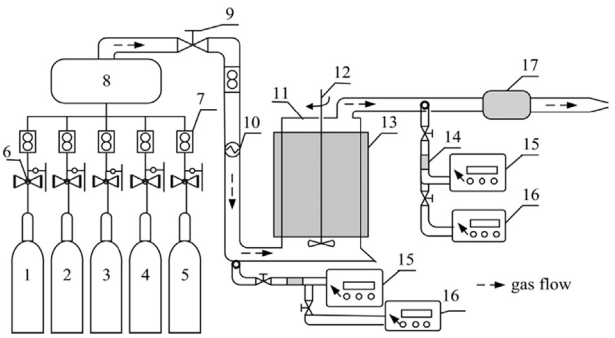

Fig. 1 – Experimental apparatus. 1-N_2 gas cylinder; 2-CO_2 gas cylinder; 3-O_2 gas cylinder; 4-SO_2 gas cylinder; 5-NO gas cylinder; 6-pressure relief valve; 7-glass-rotor flow meter; 8-buffer bottle; 9-flow control valve; 10-gas electric heater; 11-bubbling reactor; 12-stirrer; 13-water-bath heater; 14-drier; 15-infrared gas analyzer of CO_2; 16-gas analysis instrument; 17-exhausted gas processing unit.

were passed into a buffer bottle and diluted by N_2 to desired concentrations, from which, the simulated flue gas with 1 atm was formed. The total gas flow was kept around 100–500 ml/min. The gas temperature was controlled in the range of 30–80 °C by an electrical heater device. The reduction reaction occurred when simulated flue gas entered into the bubbling reactor containing KBH_4 solution. The reaction temperature was adjusted from 30 to 80 °C by an electric-heated thermostatic water bath. The solution pH was regulated by mixed acid and alkali (phosphoric acid, acetic acid, boric acid and sodium hydroxide) buffer, and measured by a pH meter (PHSJ-5, Shanghai Leici Instrument Company, China). The stirrer speed was controlled in the range of 20–30 rpm. After passing through the tail gas treatment part, the spent simulated flue gas was discharged into atmosphere.

In order to improve the validity of experimental results, the effects of influencing factors such as, KBH_4 concentration, reaction temperature and solution pH on CO_2 reduction were investigated consecutively, in which, the experiments were implemented by increasing the numerical values of each influencing factor, and then by decreasing these values. The experimental data were obtained by averaging the two measurements.

Analysis methods

An ion chromatograph (IC, Metrohm 792, Switzerland) and a Fourier Transform Infrared Spectroscopy (FT-IR, NICOLET 380, USA) were used to characterize reaction products. A multi-functional flue gas analyzer (MRU95/3 CD, Germany) was used to detect the concentrations of SO_2, NO and O_2. An infrared gas analyzer (Xibi GXH510, China) was used to determine the inlet and outlet CO_2 concentrations, from which, the conversion efficiency can be calculated according to Eq. (1)

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

where, η_{ce} represents the conversion efficiency of CO_2, %; φ_i and φ_0 are the inlet and outlet CO_2 concentrations, respectively, %.

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