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Absorption of carbon dioxide by hydrogen donor under atmospheric pressure

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ABSTRACT

Commonly, carbon dioxide (CO_2) capture and resource utilization (CCRU) covers a broad area of research with different technical challenges. Thus, more exploratory technological investigations are needed to discover new applications and reactions. In this paper, an innovative method for CO_2 absorption by sodium borohydride ($NaBH_4$) from coal-fired flue gas was developed under atmospheric pressure and moderate temperature. The effects of influencing factors, such as volume ratio of ethanol to water, $NaBH_4$ concentration, reaction temperature, solution pH, and concentrations of sulfur dioxide, nitric oxide and oxygen on CO_2 absorption were investigated. The average absorption efficiency of CO_2 was 54.06% under optimal experimental conditions, in which volume ratio of ethanol to water was 80%, $NaBH_4$ concentration was 0.439 mol L^{-1}, reaction temperature was 318 K and solution pH was 9.0. The coexisting gases of sulfur dioxide, nitric oxide and oxygen in flue gas had no significant competition or inhibition effect on CO_2 absorption. Ion Chromatography and Fourier Transform Infrared Spectroscopy analyses of products proved that the main reaction product was formate with 41.52% of the selectivity. Combined with the analysis of the electrode potentials, the mechanism of CO_2 reaction with $NaBH_4$ was proposed. Meanwhile, a comparative research of CO_2 resource utilization can provide a useful reference for developing new CCRU technologies.

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1. Introduction

In recent years, the atmospheric concentration of carbon dioxide (CO_2) has been increased rapidly due to the excessive exploitation and utilization of fossil fuels [1,2]. According to the report on trends of global CO_2 emissions in 2013, global CO_2 emission reached up to 34.5 billion tones in 2012 [3]. The investigations on major greenhouse gases such as CO_2, methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorinated compounds (PFCs) and sulfur hexafluoride (SF_6) indicate that CO_2 has the most significant effect on the rising atmospheric temperature because of its greatest emissions, therefore, it's urgent to study on the emission reduction of CO_2.

Nowadays, more and more researchers have participated in the study of carbon capture and resource utilization (CCRU) [4]. Methods currently used or developed for CCRU include but not limited to: physical and chemical solvents, various types of membranes, adsorption onto solids, cryogenic separation, and other novel technologies include ionic liquids (ILs) etc., nanoparticle organic hybrid materials, and chemical looping sorbents [5,6]. Under atmospheric pressure, CO_2 capture by alkanol amine, ammonia solutions or ILs has been widely studied and partially applied to industrial engineering [7–9]. Among the alkanol amine methods, mono-ethanolamine (MEA) is used most extensively, but the absorption efficiency of CO_2 is not high and the regeneration product is only CO_2 [10]. For the method of ammonia solutions, due to the high saturated vapor pressure and the fast evaporation rate, ammonia escape is becoming an important technical issue which causes secondary pollution and materials loss [10,11]. In addition, most technologies of CO_2 absorption are energy-intensive and are also plagued by corrosion problems, owing to the regeneration of solvent. Currently, more attention has been focused on CO_2 absorption by ILs [12]. Nevertheless, the complicated design and synthesis of high effective ILs and poor economics may be major obstacle to its industrial application and future development [13].

With the in-depth research, scholars realize that CO_2 can be considered as a valuable carbon resource. As an effective approach for the resource recycling of CO_2, CO_2 hydrogenation has become a current research hotspot [14–21]. A variety of organic and inorganic hydrogen donors, such as isopropyl alcohol [22], dimethylamine-borane [23], and ammonia-borane [24] have been used for CO_2 hydrogenation. Nonetheless, these processes can only be carried out under dozens of atmospheric pressures, and huge amounts of energy will be consumed. Besides, the poor conversion efficiency of CO_2 also becomes an important technical issue in these processes. In order to reduce energy consumption, the hydrogen donor of sodium borohydride ($NaBH_4$) for CO_2 conversion has been applied in the fields of direct fuel cells [25,26], fabrication of carbon nanotubes [27] and boron-doped porous carbon [28,29]. But the problems of high operating pressure or high temperature are still existed in these processes. Obviously, there are two problems that need to be noted in CO_2 hydrogenation running at high pressure or temperature. First, the investment cost will be raised as the equipment manufacture needs a large amount of pressure or temperature resistant metal materials. Second, the energy consumption will be significantly increased during the operation. As a consequence, it is difficult to apply the existing methods of CO_2 hydrogenation in industrial applications, and developing the technology of CO_2 utilization with low energy consumption will be greatly meaningful to CO_2 emission reduction.

Based on the excellent reducibility of $NaBH_4$, a comprehensive investigation about $NaBH_4$ reaction was carried out, from which, it was concluded that there were few reports about CO_2 absorption by $NaBH_4$ under atmospheric pressure and moderate temperature. Hence, in order to explore a new approach for the resource utilization of CO_2 at low cost, the reaction of CO_2 reduction by $NaBH_4$ under atmospheric pressure and moderate temperature was investigated in this paper. The effects of various factors, such as volume ratio of ethanol to water, $NaBH_4$ concentration, reacting temperature and solution pH on CO_2 absorption by $NaBH_4$ were studied. The investigations of sulfur dioxide (SO_2), nitric oxide (NO) and oxygen (O_2) in coal-fired flue gas were also carried out to clarify their competition or inhibition mechanisms on the reaction system. Meanwhile, the reaction mechanism was proposed on the basis of the product analysis, the electrode potentials of reactants and products. Meanwhile, a comparative research of CO_2 resource utilization was carried out. The results can provide a useful reference for developing new CCRU technologies. This work can provide an example of CO_2 utilization and a useful reference for developing new CCRU technologies.

2. Experimental

2.1. Materials

Adding ethanol and water with appropriate ratio into a beaker and adjusting solution pH from 8 to 13 by sodium hydroxide (1 mol L^{-1}) to inhibit the self-hydrolysis of $NaBH_4$, and then adding certain amounts of $NaBH_4$ at ambient temperature. Hence, the absorption solution of $NaBH_4$ was obtained. Gases were all supplied from compressed gas steel cylinders (North Special Gas Co., Ltd., China). Reagents used were analytical reagent (AR) (Tianjin Chemical Reagents Company). High purity water, with specific resistance of >18.25 MΩ/cm, was used to prepare the absorption solutions.

2.2. Experimental procedure

The key part of the experimental system (Appendix Fig. A1) is a bubble reactor (home-made) with 250 mL of the effective volume and 15.5 cm of height, and a gas blanket of micron porous core fabric is located at a distance of 1.5 cm from the bottom of reactor. During the experiments, all gases were metered through mass flow controllers (LZB, Tianjin Flow Meter Co., Ltd., China) and mixed in a buffer bottle, in which CO_2, O_2, SO_2 and NO were diluted by nitrogen gas (N_2) to desired concentrations, and then simulated flue gas with 1 atm (gauge pressure) was formed. The total gas flow was kept around 400–750 ml min^{-1}, and gas temperature was controlled in the range of 288–338 K by an electric-heated thermostatic water bath, in accordance with that of actual flue gas after desulphurization processes. The absorption reaction occurred when simulated flue gas entered into the bubbling reactor containing $NaBH_4$ solution. 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 tail gas treatment part, spent simulated flue gas was discharged into atmosphere.