



Synthesis of CuCl/Boehmite adsorbents that exhibit high CO selectivity in CO/CO₂ separation



Kanghee Cho^a, Jungsu Kim^{a,b}, Hee Tae Beum^a, Taesung Jung^{a,*}, Sang Sup Han^{a,*}

^a Climate Change Research Division, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon, 34129, Republic of Korea

^b Graduate School of Energy Science and Technology, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon, 34134, Republic of Korea

HIGHLIGHTS

- A highly selective CO adsorbent based on a CuCl/boehmite composite was synthesized.
- The adsorbent exhibited a very high CO/CO₂ separation factor.
- High separation ability is attributed to the natural properties of the boehmite.
- The thermal treatment temperature was optimized for CuCl dispersion onto boehmite.

ARTICLE INFO

Article history:

Received 7 August 2017

Received in revised form

15 November 2017

Accepted 20 November 2017

Available online 21 November 2017

Keywords:

Adsorption
Carbon monoxide
Carbon dioxide
Adsorbent
CuCl/boehmite

ABSTRACT

We developed nanoporous adsorbent exhibiting unprecedented performance in separation of toxic carbon monoxide (CO). The adsorbent was prepared by dispersing CuCl on mesoporous boehmite via thermal monolayer dispersion route. A key point of the present synthesis is dispersing optimized amount of CuCl on the boehmite at a moderate temperature to maintain the characteristics of the boehmite. We performed a systematic study to reveal that a CuCl/boehmite composite (30 wt% CuCl in total) thermally treated at 573 K was the best optimized sample for CO separation. The CuCl/boehmite had a high capacity of CO adsorption (1.56 mmol g⁻¹) and an exceedingly low capacity of CO₂ adsorption (0.13 mmol g⁻¹) under 100 kPa of each gas at 293 K. The CO/CO₂ separation factor was 12.4. To the best of our knowledge, this value is the best on record. The achievement of this work is attributed to finding a new type of suitable supporting material: boehmite. The boehmite has a high affinity to CuCl, exhibits excellent dispersion of the CuCl, and achieves a superior CO adsorption capacity. However, it has a weak interaction with CO₂. The CuCl/boehmite composite is a promising adsorbent for selective separation of CO from combustion exhaust and industrial off-gas streams.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Carbon monoxide (CO) is mainly produced by steam reforming, partial oxidation, and steelmaking processes [1,2]. In the steelmaking process, CO, which is contained in off-gas streams such as coke oven gas (COG), blast furnace gas (BFG) and Linz–Donawitz gas (LDG), is a waste product, and it is largely burned off in the form of CO₂ to recover energy [3]. However, CO can be better utilized by producing more valuable materials instead of emitting a greenhouse gas if the CO is separated from the off-gas mixtures (CO, CO₂, N₂, H₂, CH₄). For example, CO is used for the production of acetic

acid, polycarbonate, isocyanates for polyurethane, and various specialty chemicals [4]. Therefore, the separation and production of high purity CO is gaining much attention and is of immense importance from the industrial and environmental points of view.

Various technologies are used for CO separation, including cryogenic distillation, absorption, and adsorption processes [5,6]. Cryogenic distillation has been widely used for large-scale separation of CO, but it is a highly energy-consuming process. The separation of CO from gas containing N₂ is economically disadvantageous because of their similar boiling points [2]. In an absorption process such as COSORB, a CuAlCl₄/toluene solution selectively absorbs CO at high pressure and desorbs CO under mild conditions [2]. It is known that the COSORB process delivers both a high purity and a high yield of CO [5]. However, the COSORB process has an environmental issue in disposing of the spent solvent and the dis-

* Corresponding authors at: Climate Change Research Division, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon, 34129, Republic of Korea.
E-mail addresses: tjung@kier.re.kr (T. Jung), sshan@kier.re.kr (S.S. Han).

advantage of an instability of Cu(I) ions, which are easily converted to Cu(0) and Cu(II) [6].

Adsorptive separation, such as the pressure swing adsorption (PSA), is the most promising method of CO separation because the process is relatively simple. This process requires low energy consumption and low cost for process operation. Moreover, it is known that the purity and yield of CO by the adsorptive separation process are high. It has been reported that Cu(I) ions on porous supports strongly bind CO molecules by π -complexation. The s -orbitals of Cu(I) ions can form σ bonds with π orbitals of CO molecules, and π back-bonding is simultaneously formed between d -orbitals of Cu(I) ions and antibonding π -orbitals of CO molecules [7,8]. Using the π -complexation bond that can be formed between the adsorbent and adsorbates, it has been successfully used for olefin/paraffin separation, CO separation, and desulfurization [7,9].

The adsorption capacity of CO is an important factor for the selection of CO-selective adsorbents to achieve high productivity of CO in the PSA operation. In addition, CO/CO₂ selectivity plays a vital role in increasing product purity since the composition of LDG is 60–67% CO, 16–18% CO₂, 16–22% N₂, and trace gases such as O₂ and H₂ [10,11]. It is also known that BFG is mainly composed of 20–30% CO, 16–25% CO₂, and 44–60% N₂ [12]. Nanoporous materials such as zeolites and metal-organic frameworks are used for adsorbents but bare supports normally have low CO/CO₂ selectivity. For separation of CO, dispersing-active species Cu(I) salts on porous materials has been applied for the preparation of CO-selective adsorbents [13]. In this case, CuCl-type adsorbents can exhibit an enhanced adsorption capacity of CO by π -complexation but reduced adsorption capacity of other gases such as CO₂ and N₂. Therefore, the CuCl dispersed on various kinds of porous materials such as zeolites, activated carbon, and silica/alumina have been suggested for selective adsorption of CO [7,13].

Xie et al. [1] prepared CuCl/NaY and CuCl/13X adsorbents by a thermal (spontaneous) monolayer dispersion method. They physically mixed zeolites and CuCl powder and heated the mixture to a certain temperature between the Tamman's temperature (the temperature at which the mobility and reactivity of the molecules in a solid become appreciable) and the melting point of CuCl. They found that the thus prepared adsorbents had a higher CO adsorption capacity than CO₂ adsorption capacity, and the adsorbed amounts of CH₄, N₂, and H₂ were almost negligible. Gao et al. [6] also prepared CO-selective adsorbents by reducing Cu(II) to Cu(I) in CO after dispersing a monolayer CuCl₂ onto NaY. Similarly, they found that the CO adsorption capacity of the CuCl/NaY adsorbent was higher than that of bare NaY, and the adsorption amount decreased in the following order: CO > CO₂ \gg CH₄ > N₂. Although the CO/CO₂ selectivity increases by dispersing CuCl onto the porous supports, it is necessary to further improve the CO/CO₂ selectivity. However, it is quite difficult to increase the CO/CO₂ selectivity in a zeolite-based adsorbent because of several intrinsic problems of the zeolite nature, such as a low size-selective sieving effect for CO (3.76 Å) and CO₂ (3.3 Å) and a high adsorption capability of CO₂ molecules in small zeolitic micropores.

Hirai et al. [14] prepared copper(I) halide-loaded activated carbon (AC) adsorbents by an impregnation method and reported that the CuCl/AC adsorbent had a higher CO adsorption capacity than CuBr/AC and CuI/AC. Tamon et al. [2] studied various kinds of AC-supported transition metal chloride adsorbents and found that the impregnation of CuCl into AC effectively increased the CO adsorption capacity. Huang et al. also synthesized a CuCl/AC adsorbent via thermal monolayer dispersion and reported that CO/N₂ selectivity of the adsorbent increased with an increasing CuCl content [15]. Ma et al. [16] prepared CuCl/AC by impregnating CuCl₂ and Cu(HCOO)₂ and the consequent reducing Cu(II) salts to Cu(I) under N₂, CO or a reduced atmosphere. They reported that the adsorbed amount of CO was much higher than those of CH₄ and N₂. However, most

of the results from the above-mentioned CuCl/AC adsorbents were neither focused on CO/CO₂ separation nor was the CO/CO₂ selectivity large. That was attributed to the high CO₂ adsorption capacity of the AC support itself as in the case of zeolite supports.

In order to increase the CO/CO₂ selectivity, it is necessary to find other types of suitable supporting materials that have low adsorption capability for CO₂. There have not been many studies that have explored adsorbents that exhibit low CO₂ uptake ability, perhaps due to the recent research trend of developing only highly-performing CO₂ adsorbents. Our research began with the idea of finding low CO₂-uptake supporters. We expected that nanomaterials with mesopores rather than small micropores, a thin framework and a weak affinity to CO₂ molecules would be more suitable than hydrophilic microporous zeolites or AC.

There have been several reports on using mesoporous alumina or mesoporous silica as supporting materials for CuCl. Golden et al. [17,18] prepared CuCl/alumina by impregnation of CuCl₂ and consequent reduction of Cu(II) to Cu(I) under CO/H₂ flow. Although the CO working capacity increased with the CuCl content, CO/CO₂ selectivity was not considered in their report [7,18]. Wang and Lin [19] prepared CuCl-supporting γ -alumina adsorbents by impregnation of CuCl using an ammonia solution as a solvent. Wang et al. [8] prepared CuCl/MCM-41 and CuCl/SBA-15 adsorbents by thermal monolayer dispersion. Recently, Yin et al. [20] synthesized silica-coated Cu₂O/SBA-15 by thermal monolayer dispersion and consequent auto-reduction at high temperature. The above studies reported that CO/N₂ selectivity is very high for CuCl-supported on mesoporous alumina or mesoporous silica. Nevertheless, the CO/CO₂ selectivity was not mentioned or it was reported to be insufficient for CO separation from CO₂-rich off-gas mixtures such as BFG and LDG.

In this study, mesoporous boehmite was tested as a supporting material for CuCl for preparation of a highly selective CO adsorbent that exhibited a larger surface area than conventional γ -alumina and a CO₂ affinity lower than γ -alumina and mesoporous silica. The CuCl was supported on the mesoporous boehmite via thermal monolayer dispersion. During this step, it was important to maintain the large surface area and the surface property of the mesoporous boehmite. The physical properties of the thus synthesized adsorbent were characterized by powder X-ray diffraction (XRD), scanning electron microscopy/Energy-dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), and the Brunauer-Emmett-Teller (BET) method. In addition, the CO/CO₂ separation factor of the synthesized materials was systematically investigated at room temperature. For this study, CO and CO₂ adsorption isotherms were measured by a volumetric method.

2. Experimental

2.1. Preparation of adsorbents

The adsorbent was prepared using the thermal monolayer dispersion method as reported elsewhere [1]. High purity synthetic boehmite was dried in a vacuum oven at 423 K overnight before the thermal monolayer dispersion of CuCl. Boehmite and CuCl (Aldrich, 97%) were mixed thoroughly and the mixture was placed in a quartz tube for heat treatment in a vacuum at various temperatures. After heating the tube in a furnace for 24 h, the adsorbent was obtained.

2.2. Adsorbent characterization and adsorption measurements

The surface area of bare boehmite and the CuCl-loaded adsorbent, which were thermally treated at different temperatures, was assessed by BET (Tristar 3020, Micromeritics) using N₂ adsorption at the liquid N₂ temperature. Before the measurements, the

Download English Version:

<https://daneshyari.com/en/article/6969500>

Download Persian Version:

<https://daneshyari.com/article/6969500>

[Daneshyari.com](https://daneshyari.com)