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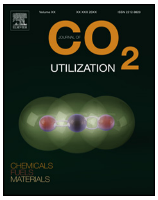

A new catalytic opportunity for waste materials: Application of waste slag based catalyst in CO_2 fixation reaction

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ABSTRACT

Iron and steel industry is one of the most energy-intensive industries, consuming 5–6% of the world's total energy consumption and emitting 5–7% of total world CO_2 gas emissions. Large volume of CO_2 emitted from iron and steel industry makes a significant contribution to global warming and climate change. Blast furnace slag (BFS), a high volume mineral waste discharged from iron and steel making processes, can potentially be used as an abundant and low-cost precursor for synthesizing active materials of catalytic interest that utilize the emitted CO_2 in synthetic chemistry. In this study, we demonstrate that a Ca-based layered double hydroxide (LDH) compound can be synthesized from BFS through a facile synthetic procedure, and the thus synthesized material acts as a solid base catalyst that efficiently catalyzes the cycloaddition reaction of epoxides with atmospheric pressure of CO_2 to give five-membered cyclic carbonates. The strategy proposed in this study would be one of the possible approaches that contribute to both efficient utilization of CO_2 and waste management problems lying in iron and steel industry.

1. Introduction

Iron and steel industry is one of the most energy-intensive industries, consuming 5–6% of the world's total energy consumption and emitting 5–7% of total world CO_2 gas emissions [1–5]. In iron and steel making processes, CO_2 is mainly produced as a result of (i) reduction of iron ore with coke in a blast furnace to produce pig iron as a main product and (ii) decarbonisation of limestone ($CaCO_3$) and dolomite ($MgCO_3$) which are added as fluxing materials together with coke for stripping the oxygen and other impurities from iron ore [1,2]. Production of every ton of steel produces about 2200 kg of CO_2 on a world average (1800 kg of CO_2 for many developed countries) [1,2]. Given a global crude steel production of 1400 Mt per year, the total CO_2 emissions at least amount to approximately 2.5 Gt, and the CO_2 emission from this industry is anticipated to further increase as this trend continues [6,7]. As witnessed over the last century, the increasing CO_2 concentration in the atmosphere has been regarded as a leading contributor to global warming and climate change. The atmospheric CO_2 level is anticipated to increase over the current concentration of approximately 395 ppm in the near future as fossil fuels remain the major source utilized to meet global energy demand and unless advanced CO_2 mitigation technologies are rapidly deployed [3,4,8–11]. Reduction of the CO_2 emission into the atmosphere has been an urgent and critical concern in both academic and industrial research communities, and accordingly significant research has recently focused on development of materials and technologies/processes suited for CO_2 capture, storage and utilization (CCSU) and for improving the energy utilization efficiency [12–19].

In iron and steel industry, technologies for reducing CO_2 gas emission and for enhancing energy efficiency over the iron and steel making processes have extensively been developed; for example, in the short-term, energy-saving or recycling technologies (e.g. recycling steel scraps as secondary sources, recycling slag and sludge as fluxing materials in steel making process to replace limestone) as well as increasing the use of renewable energy (such as biomass fuels) instead of the conventional reducing agents (coke, coal, etc.) [1,2]. In the long-term, in-process and post-combustion CO_2 capture and its permanent or semi-permanent storage (CO_2 capture and storage; CCS) have currently been considered as effective mitigation technologies for climate change [1–4], and the technical feasibility and the economic and environmental assessments of the processes have been believed to be promising [20]. However, CCS technology is still under development [21], and in an ideal CCS technology currently

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Table 1
Types and amounts of products generated from coal-fired power plants and iron and steel making plants.

Plant	Iron and steel making plant	Coal-fired power plant
Input	Iron ore Limestone ($CaCO_3$), dolomite ($MgCO_3$) (fluxing material) Coke, coal (reducing reagent)	Coal, oil, natural gas, biomass
Output	Pig iron (1026 Mt globally in 2010)[a] Crude steel (1417 Mt globally in 2010)[a]	Electricity
Byproduct	Blast furnace slag (230–280 Mt globally in 2008)[b] Converter/refining slag (130–200 Mt globally in 2008)[b]	Fly ash (430 Mt globally in 2003)[d]
CO_2 emission	2.5 Gt globally in 2009[c] (5–7% of total CO_2 emission)	11.8 Gt globally in 2005 (40% of total CO_2 emission)

[a] Data from Ref. [6].
[b] Data from Ref. [25].
[c] Data from Ref. [7].
[d] Data from Ref. [36].

proposed, the captured CO_2 is finally sequestered in a reservoir, such as depleted oil and gas reservoirs, deep oceans, and deep aquifers, for an indefinite period without any benefits [4,12,20,22]. In terms of efficient utilization of CO_2, the extracted and concentrated CO_2 generated from such large stationary sources should be subjected into "on-site" usages and should be used for more productive purposes, such as feeding greenhouses, feeding enclosed algae installations for biofuel production, and supplying as a C_1 feedstock for chemical and polymer production, where continuous supply of a large volume of concentrated CO_2 gas is required [5,12]. Thus, further breakthrough technologies that efficiently capture and utilize CO_2 have been required in steel industry.

Iron and steel making industry plants produce not only huge amount of CO_2 but also high volume of byproduct, together with pig iron and steel as main products. Types and amounts of products generated from iron and steel making plants are tabulated in Table 1, together with those from coal-fired power plants as comparative data. The solid byproducts generated during iron and steel manufacturing are mainly in the form of slag. There are different types of steel slag, each one named for the process from which they are generated, e.g. blast furnace slag (BFS), basic oxygen furnace slag (BOF), electric arc furnace acid slag (EAF) and ladle furnace basic slag (LF), the former one is also called iron-making slag and the latter three are also called converter/refining slag [23,24]. Approximately 290 kg of BFS is generated per ton of pig iron, and approximately 110 kg of BOF is generated to produce one ton of crude steel. The annual world production of slag from iron and steel industries reaches almost 400–500 Mt, which accounts for approximately one third of the global emissions of inorganic waste, and is anticipated to further increase as this trend continues [23,25]. Due to their mineral compositions, iron and steel making slags have been mostly recycled as secondary sources for hydraulic cement, concrete aggregate, and pavement materials in civil engineering work, or in part disposed of by landfilling and dumping into sea without any profits [23–27]. However, the heavy metal ions in the slags may have adverse effects on human health, aquatic life and the overall ecosystem via a potential seawater/groundwater contamination, and the urgent problems such as the shortage of storage sites and severe environmental regulations are matters of great concern as well. Hence, development of new and advanced recycling processes for waste slags in an energy-saving and environmentally-friendly way has been required to promote sustainable development of iron and steel industry [28].

In recent years, driven by both economic and environmental considerations, studies on recycling processes for waste materials have been attracting much attention. High volume waste materials resulting from large scale industrial sources particularly afford opportunities in terms of catalysis [29]. To date, a number of reports detailing the application of wastes to the preparation of catalysts have been reported, in which they are directly applied, in some instances, as catalysts themselves, in others they are used as precursors or alternative sources for the synthesis of active catalysts [30–35]. For example, fly ash, a solid waste residue produced from coal, oil and biomass combustion in fossil fueled power plants, has extensively been investigated to be utilized as adsorbent, heterogeneous catalyst, catalyst support as well as feedstock for zeolite synthesis exploiting its high silica and alumina content (see also Table 2) [36–41]. One of the crucial drawbacks for recycling fly ash is the potential influence of compositional variation on the performance of the products, because the chemical compositions of fly ashes are strongly dependent upon the fuel sources being burned (coal, oil, natural gas and biomass, etc.) and the combustion technology applied [36]. Compared to fly ashes, the chemical composition of iron and steel making slags is less variable and is especially rich in CaO that by nature show strong basicity. These fundamental backgrounds of iron and steel making slags potentialize them to be used as low-cost and abundant raw materials for preparing a solid base catalyst [33,34].

Motivated by the above situations, we herein propose a new approach that would potentially contribute to both the efficient CO_2 utilization and waste management problems associated with iron and steel industry. The strategy developed in this study is comprised of two parts: (i) conversion of waste slag into a Ca-based solid base catalyst and (ii) application of the slag-made catalyst in CO_2 fixation reaction (Scheme 1). Among several kinds of waste slags discharged from iron and steel making processes, BFS was chosen as a raw material primarily because of its larger amount produced than those of other types of slags [23,25]. As listed in Table 2, BFS mainly consists of CaO, SiO_2, Al_2O_3 and MgO as well as slight amount of metallic elements such as Fe, Ti and Mn, whereas

Table 2
The chemical composition of BFS and fly ash (wt%).

Waste	CaO	SiO_2	Al_2O_3	MgO	FeO	TiO_2	MnO	LOI[c]	Others
Blast furnace slag[a]	40.09	34.58	14.78	5.29	1.53	0.78	0.27	–	2.68 (S, Na_2O, etc.)
Fly ash[b]	1.7	61.8	27.9	0.3	2.6	1.0	–	2.0	4.7 (P_2O_5, Na_2O, K_2O, etc.)

[a] BFS used in this study. Determined by ICP analysis.
[b] Data from Ref. [26]. May vary depending on the fuel sources being burned (coal, oil, natural gas and biomass, etc.) and the combustion technology applied.
[c] Loss on ignition.