ANNOTATION

on the thesis for the degree of Doctor of Philosophy (PhD)
on specialty 6D074000 - "Nanomaterials and nanotechnology"

of

ZHUMAGALIYEVA ASSEM NURBERGENOVNA

PRODUCTION AND TESTING OF CARBONIZED RICE HUSK-BASED NANOCOMPOSITES FOR CAPTURING OF CARBON DIOXIDE

General description of the work. The thesis is devoted to produce and testing carbon-based nanocomposite containing iron-oxide nanoparticles for carbon dioxide adsorption in post-combustion flue-gas conditions. In this work, in order to collect new data about CO_2 adsorption by nanocomposite materials of the Fe_3O_4-C system were tested in a laboratory static microreactor under the conditions of flue gases after combustion.

Carbonated biomass (rice husk, RH) were used as the supporting carbon matrix. The effect of base leaching on carbonated rice husk (cRH) was also investigated.

Importance of the work. CO_2 emissions are the main factor influencing the global warming. To reduce greenhouse gas emissions the use of gas capture technologies at point sources of pollution, such as coal-burning plants and other electricity generation, large industrial facilities etc. has been proposed and, in many cases, implemented. In this framework, CO_2 capture and sequestration (CCS) can be pursued by three major approaches: pre-combustion capture, oxy-fuel combustion and post-combustion capture. Post-combustion on solid sorbents is the one of advantageous CO_2 capture strategy. Effectiveness of this process primarily driven by economics, because it not implicate significant modifications to the combustion process technologies currently used. The use of solid sorbents offers remarkable advantages over the other separation methods, because it offers great capacity, selectivity, easy handling and reduced energy for regeneration. The performances of solid sorbents towards CO_2 absorption are often studied at high pressures. It was found that materials with a large capacity for CO_2 uptake at high pressure often do not perform well at low pressure and in particular it was established that at low pressure as in post-combustion conditions (1 bar and CO_2 10–15% volume the CO_2 uptake capacity) the CO_2 uptake is influenced primarily by the chemistry of the sorbent surface (chemical functional groups) and by specific pore metrics.

Materials with a distinctive surface chemistry could find large applications in adsorption technologies. Recent studies of CO_2 adsorption on low-cost hydroxylated metal oxide surfaces strongly encourage the possible use of metal oxide as sorbents. Magnetite (Fe_3O_4), a low cost iron metal oxide, biocompatible and non-toxic for human body have been applied in a variety of fields and recently

also in gas sorption. Magnetite, like other metal oxides exhibits active sites exposed at the surface which can interact with gaseous molecules. The problem of predisposition to the agglomeration process of the particles is turned to use a carbonaceous matrix, which helps overcome this disadvantage. In this work cRH was used as carbon matrix working as support for the preparation of composite materials containing iron oxide particles as active nanomaterials toward CO_2. This material has a great potential for technological applications since it can be converted into different type of sorbent materials through a variety of thermochemical conversion processes. The production of sorbent materials starting from RH can mitigate different environmental issues: the use of agricultural wastes reduces disposal issues and the valorization of end-of-life materials as sorbents materials (CO_2 or heavy metals from wastewater) faces remediation issues.

A feature of this scientific study is also that all adsorption manipulations were carried out in a laboratory breakthrough microreactor with a fixed bed, the conditions for all experiments were typical for flue-gases at room temperature and normal atmospheric pressure.

Purpose and objectives of the work. Production of carbon-based nanostructured composites containing iron oxide particles, structural and morphological characterization of the produced materials and adsorption properties evaluation for CO_2 capture applications in post-combustion flue-gas conditions.

To achieve the goal it is necessary to solve the following tasks:

− To investigate structural characterization of carbonized rice husk used as carbonaceous matrix in nanocomposites;

− To synthesize composite materials based on carbonized rice husk coated with magnetite particles (cRH-FMs), magnetite nanoparticles (cRH-nFM);

− To evaluate of the optimal parameters for alkaline treatment of cRH to investigate the dependence of CO_2 adsorption capacity with the surface and structural characteristics of alkali-treated cRH materials;

− CO_2 sorption performances evaluation of the obtained materials by breakthrough experiments on a laboratory-scale fixed-bed micro-reactor under post-combustion flue-gas conditions;

The main provisions of the thesis, which are submitted for defense:

1. Carbonized rice husk has high CO_2 uptake up to 11.26 mg/g under post-combustion flue-gas conditions. The sorption capacity of cRH significantly increases to 29.2 mg/g by leaching with an increase in the concentration of the base NH_4OH to 28% in the aqueous solution.

2. Prevention of agglomeration of iron oxide particles in a composite material based on cRH and nanoporous magnetite nFM, in a ratio of 67:33 co-precipitated with TMAOH, effectively increased the sorption capacity to 15.6 mg/g, which exceeds individual indicators of the components by 38% and 13%, respectively. This effect is due to an increase in the volume of microspores up to $3.81*10^{-2}$ cm^3/g and a good synergism between the chemisorption of iron oxide nanoparticles and the physical adsorption of carbon in cRH.

3. cRH treated with NaOH solution increases the carbon content up to 80% and the specific surface area of the material up to 431 m^2/g, which enhance physical sorption and increase the sorption capacity up to 21.9 mg/g.

4. The sorption capacity cRH of the treated NH_4OH increases to 29.2 mg/g due to chemisorption. This effect refines the saturation time of the sorbent up to 25 s with partial removal of silica, which shows an increase in the saturation time of the sorbent up to 25 s with partial removal of silica.

Research object: synthesis and characterization of carbon-based nanocomposites for carbon dioxide capture applications.

Research subject: investigation of the structure and the physicochemical properties of nanocomposite materials based on carbonized rice husk and study of the influence of material synthesis parameters on the CO_2 adsorption performances.

Methods of research: To reach the established purposes and to solve the above reported objectives, wet-chemistry approaches have been selected for the syntheses of the materials and the following instrumental methods for their structural characterization have been used: elemental analysis (EA), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), inductively coupled plasma–mass spectrometry (ICP-MS), Brunauer–Emmett–Teller analysis (BET), scanning electron microscopy (SEM), energy dispersive analysis (EDAX), x-ray diffraction (XRD), atomic force microscopy (AFM).

For estimating the materials adsorption capacity, a laboratory-scale fixed-bed micro-reactor has been used.

Scientific novelty of the work lies in the fact that for the first time nanostructured composite materials based on cRH supported with iron oxide obtained by co-precipitation method investigated in typical post-combustion flue-gas conditions for determination CO_2 adsorption capacity.

1. Nanostructured composite materials were synthetized by coating cRH with magnetite particles (cRH-FMs) and magnetite nanoparticles (cRH-nFM) and explored its CO_2 adsorption capacity in typical 1 atm, 3-15% volume CO_2 post-combustion flue-gas conditions;

2. Systematic investigation on the effect of different alkaline treatments for the removal of cRH inorganic components has been carried out , also CO_2 capture performances have been evaluated; maximum sorption capacity achieved 29.2 mg/g for cRH treated by NH_4OH;

3. The influence content of magnetite particles in carbonized rice husk composites on CO_2 adsorption capacity has been established. It was found that an increase of CO_2 sorption capacity is associated with a certain presence of both micro and mesopores in composites.

4. It was assessed that the CO_2 capture sorption mechanism of the produced composites is intermediate between a pure chemisorption and a pure physisorption interaction

Theoretical significance

The theoretical significance of the investigation relies in the determination of the optimal parameters for the production of alkali treated cRH sorbents and composite materials based on cRH and magnetite with CO_2 capture performances suitable for practical application in post-combustion conditions.

It is established the optimal mass ratio of cRH and nanosized magnetite to obtain a synergistic effect between the two components with the aim of achieving better CO_2 uptakes. The obtained results were discussed taking into account the influence of the specific surface area, pore size distribution and other structural characteristic influencing the CO_2 adsorption by a solid sorbent.

Practical application

The practical significance lies in the fact that the developed composite materials based on carbonized rice husk have the prospect of being used in practical applications as adsorbent for carbon dioxide capture and sequestration technology as low-cost solid sorbents in post-combustion conditions. Moreover, the production of low-cost CO_2 solid sorbents starting from cRH represents an encouraging possibility to face environmental problems related to the disposal of rice husk, since it is a very abundant and available agricultural waste.

Approbation of the work. The results of the dissertational work have been reported and discussed at the following international and regional scientific and technical areas: XXXIX Meeting of the Italian Section of the Combustion Institute, Naples, Italy, 2016; International Conference on Applied Mechanics, Mechanical and Materials Engineering, Xiamen, China, 2016; Joint IX International Symposium «Physics and Chemistry of Carbon Materials/Nanoengineering» and International Conference «Nanoenergetic Materials and Nanoenergetics», Almaty, Kazakhstan, 2016; International Scientific-Practical Conference "Modern problems of biotechnology: from laboratory research to production", Almaty, Kazakhstan, 2016; III International Farabi Readings, Almaty, Kazakhstan, 2016; I Conference of Students and Young Scientists "Chemical Physics and Nanomaterials", Almaty, Kazakhstan, 2016; V International Student Forum “Green bridge through generations”, Almaty, Kazakhstan, 2016; II Conference of Students and Young Scientists "Chemical Physics and Nanomaterials", Almaty, Kazakhstan, 2017; Tenth Mediterranean Combustion Symposium, Napoli, Italy, 2017; X International Symposium “The physics and chemistry of carbon and nanoenergetic materials” Almaty, Kazakhstan, 2018.

Part of the experimental work has been carried out at Institute for Research on Combustion and University of Naples Federico II, Naples, Italy under the supervision and support of the foreign scientific consultant.

The author’s personal contribution consisted in: the execution of the experimental activities devoted to the synthesis and the characterization of the materials object of the dissertation work; the interpretation and discussion of the results; the preparation of articles, thesis and reports. Purposes and objectives, the experimental work planning, the interpretation of the results and the general provisions for the defense were discussed with both scientific consultants.

Publications. The general results of the thesis were published in 12 printed works, which 1 is included in the Scopus database (published in Combustion Science and Technology journal with 1.73 impact factor), 1 patent for a utility model, 3 is published in journals recommended by the Committee for Control in Education, Science of the Ministry of Education and Science of the Republic of Kazakhstan and 7 publications in international and regional conferences bulletins.

Scope and structure of the work. The thesis is represented in 106 pages of printed text and contains 62 figures and 26 tables. The work consists of an introduction, a review of the literature, a description of the objects and methods of research, the results and their discussion, conclusion, appendix, a list of used sources from 163 references.