Fuel 119 (2014) 323–327

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Short communication

Development of copper impregnated porous granulates for chemical-looping combustion

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ARTICLE INFO

Article history:
Received 15 December 2012
Received in revised form 15 August 2013
Accepted 28 November 2013
Available online 8 December 2013

Keywords:
Bed material
Microstructure
Impregnation
Looping efficiency
Attrition resistance

ABSTRACT

Highly porous supports based on clay, alumina and diatomite were developed using extrusion method. By combination of diatomite and clay, a macrostructure was obtained, whereas with alumina composition a mesoporous structure occurred. Composites based on alumina and diatomite result in a systematically tunable macrostructure. Therefore it was possible to increase the total pore volume and achieve a tailored microstructure from the meso- to macropore range. To verify the workability of the developed supports for chemical-looping combustion (CLC), impregnation with 1.5 M copper nitrate trihydrate was performed on selected samples. Presence of mainly CuO and Cu_2O phases were obtained in silica based samples (clay, diatomite), whereas $CuAl_2O_4$ spinel phase dominated in samples with high alumina content. CLC performance was verified by thermogravimetry using $CO + N_2$ or $O_2 + N_2$ gases. The highest performance could be achieved with the γ-alumina–diatomite composite support material.

1. Introduction

Energy production by using combustion processes will still be a big issue in the future. Either fuel based on oil or natural gas, which is expected to reach its reserve limit in 40–60 years, coal, or renewable energy sources like wood or plants can be used. The main drawback of energy production by combustion power plants is the anthropogenic CO_2 emissions of about 40% [1].

Current CO_2 capture technology is based on amine scrubbing, which can remove CO_2 from exhaust gas including nitrogen and hydrogen [2]. This technique is however known to reduce the efficiency of a power plant down by 26%. Additional gas cleaning units to remove impurities such as SO_x and NO_x are necessary. A new envisaged technique is the chemical-looping combustion (CLC) that either can be used for hydrogen or synthetic gas (syngas composed of CO, CO_2 and H_2) production, or for the direct combustion of solid fuel (such as biomass or coal) without NO_x formation. It is envisaged to use this technique for conversion of coal or biomass to synthetic natural gas (SNG) via gasification and methanation, coupled with CO_2 capture.

Chemical-looping combustion is considered as one of the most promising techniques for CO_2 separation of fossil fuel combustion. It involves the use of an oxygen carrier, which transfers oxygen from an air reactor to a fuel reactor for combustion, without direct contact between the fuel and the air [3] and a support material which gives the necessary mechanical properties. The oxygen carrier is frequently based on Cu, Ni, Fe, and / or Mn oxides. Gases, such as CO, H_2, CH_4 are usually chosen as a fuel. The almost pure stream of CO_2 can be separated for CO_2 storage by water condensation with only a small loss of energy [4–7]. The support material requires a good attrition resistance because of the impacts granulates/granulates and granulates/walls involved by the gas velocity in the reactors [8]. The materials which are most widely used are SiO_2, TiO_2, ZrO_2, Al_2O_3 or YSZ. De Diego reported that CuO without support lost 90% of its initial reactivity after only three looping cycles, while no lost was observed with the use of a silica support [9]. The oxygen carrier can tend to agglomerate because of sintering and deactivate because of the presence of ashes. A porous support material requires a highly interconnected open porosity to facilitate the oxygen carrier impregnation, and a high specific surface area, low neck and ink-bottle content to optimize the exchange of oxygen gas. It also requires a high attrition resistance to withstand the mechanical and chemical stresses during its use in a fluidized bed reactor.

In this work, microstructure was tuned from meso- to macropore range using different material compositions, namely clay-diatomite, alumina and alumina-diatomite composites. The different porous substrates were investigated to determine their influence on Cu impregnation and oxygen carrier reactivity with the different applied gases.

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http://dx.doi.org/10.1016/j.fuel.2013.11.063

2. Experimental

2.1. Processing of support material

2.1.1. Development of diatomite-clay support

Two diatomite filter aids Filter Cel and Super Cel (Celite, World Minerals Inc., USA) with specific surface areas of 8.8 and 2.7 m^2/g, median particle sizes of 14 and 15 μm, respectively and median pore sizes of 2.5 and 3.5 μm (supplier data) and kaolin EKA-S (Amberger Kaolinwerke, Germany) were used to achieve substrates with macroporous structure by extrusion process. Dry powders were premixed for 3 min in a planetary mixer before adding an emulsion of deionised water and oil. After mixing, the feedstocks were shaped with a piston extruder (Type 232 16 DT-HS, Loomis, Germany) at a pressure of 40–50 bar through a die with an orifice of 500 μm. The extruded materials were dried for 3 days at 60 °C before being ground and sieved into granulates with a size from 180 to 500 μm. Finally, granulates were sintered in air at 1100 °C for 3 h in a furnace (PY 12H, Pyrotec) with a heating rate of 110 °C/h. Further information on these granulates were previously reported [10–12]. These granules were studied for chemical looping desulfurization too with the use of Mn instead of copper, as presented in this study.

2.1.2. Development of γ-alumina support

Pseudo-boehmite G-250 (BASF, USA) with an agglomerate size d$_{50}$ of 60 μm was selected for this study to produce supports with a mesoporous microstructure. The material has a specific surface area of 295 m^2/g and considering spherical particles, a primary particle size of 9 nm was calculated. Dry powder was mixed in a high shear mixer (Janke & Kunkel, IKA Labortechnik RE 162/P Analog, Germany) with 82 wt.% of solid content and was peptized with a 1.87 M acetic acid solution. Cylindrical extrudates (Ø = 1.5 mm) were produced using a capillary rheometer (Rosand RH7, Malvern, Germany). After drying step (48 h at room temperature), the extrudates were calcined in air at 850 °C with a dwell time of 2 h. Granulated support material with a size between 180 and 500 μm were afterwards obtained by grinding and sieving. The process was previously reported [13].

2.1.3. Development of γ-alumina–diatomite support

To tailor the porosity of the support material in the meso- to macropore range, pseudo-boehmite G-250 (BASF, USA) and the diatomite powders mentioned previously (Celite, World Minerals Inc., USA) were used. Dry powders were first mixed in a high shear mixer (Janke & Kunkel, IKA Labortechnik RE 162/P Analog, Germany) for 2 min at 25 rpm. Afterwards, a 1.87 M acetic acid solution and organic binders were added to the mixture. Total compounding step lasted 1 h. The feedstock was then extruded through a 1.5 mm diameter die using a capillary rheometer (Rosand RH7, Malvern, Germany) and dried for 48 h at room temperature. Finally, the extrudates were heated up to 850 °C with a dwell time of 2 h, granulated and sieved between 180 and 500 μm.

2.1.4. Impregnation of support material

Granulates were impregnated for 14 h in a 1.5 M copper nitrate trihydrate solution. The liquid to powder ratio was fixed to 12.5 mL g^{-1}. The material was then filtered and dried at 80 °C during 24 h. The impregnated cylindrical granulates were calcined at 550 °C for 30 min in order to decompose it into copper oxide, as described by Forero et al. [14]. A thermal treatment at 850 °C for 1 h in air was followed to stabilize the oxygen carrier.

2.2. Characterization

2.2.1. Microstructure investigations

Total porosity and average pore size were evaluated by a mercury porosimeter (Pascal 140/440, Thermo Fisher, Germany). Mesoporosity was determined by nitrogen sorption at 77.4 K with a BET device (type SA 3100, Coulter, Switzerland), using the Barrett–Joyner–Halenda (BJH) model based on the Kelvin–Laplace equation [15] from the nitrogen desorption plot. Samples for both measurements were dried 14 h at 180 °C in order to drive off any physisorbed water.

2.2.2. Crystallographic phase composition

For the chemical phase analysis, an X-ray powder diffractometer X′Pert Pro PW3040 (PAN analytical, Switzerland) with Cu target (K_α, λ = 0.15406 nm), radiation of 45 kV and 40 mA was used.

2.2.3. Chemical-looping combustion investigation by TG analysis

Thermogravimetry (TG) was performed with a TGA/SDTA851 (Mettler Toledo Corporation, Switzerland) with the following setup: alumina crucibles, filling up to 75 vol.% of the pan and 50 cm^3 min^{-1} gases flow. According to the fact that granule size and shape were constant, similar packing density can be assumed. Therefore, the mass transport will be dominated by microstructure of the porous granulates and interaction between the copper phases and the different support materials. The reducing gas was composed of 10% CO (purity ±2%) and 90% N$_2$, while the oxidizing gas was composed of synthetic air (20% O$_2$ (purity ±1% O$_2$) and 80% N$_2$). At 850 °C, oxidizing and reducing gases were interchanged manually every 20 min to stabilize the redox state of the oxygen carrier. Between each gas, nitrogen was flushed during 5 min to clean the chamber.

Table 1
Porosity determined by mercury porosimetry analyses of not impregnated and impregnated samples (calcined at 850 °C).

	Not impregnated		Impregnated		
	Porosity (%)	SSA (m^2/g)	Porosity (%)	SSA (m^2/g)	Weight gain[a] (%)
		Diatomite-clay substrate			
48 vol.% clay_1100 °C	68	2	54	1	34.2
		γ-Alumina substrate			
0 vol.% diatomite	61	153	54	105	36.2
		γ-Alumina–diatomite substrates			
19 vol.% diatomite	46	36	51	17	28.2
84 vol.% diatomite	71	17	38	15	30.1

[a] Weight gain after impregnation and drying at 80 °C for 24 h.