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Chemical looping capabilities of olivine, used as a catalyst in indirect biomass gasification

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ABSTRACT

Indirect biomass gasification systems consist of two reactors: an oxidation reactor and a gasification reactor. A bed-material is used to transfer heat from the oxidation to the gasification reactor. Olivine has been widely studied as a reactive bed-material for this process. The iron in olivine can act as a catalyst for the decomposition of tars, produced during the gasification process. Moreover, iron is capable of transferring oxygen to the gasification reactor. In this study, we elucidate the role of iron in this chemical looping process. Mössbauer spectra show that during oxidation in O_2/Ar at 750 °C, iron segregates out of the olivine matrix forming free iron oxide phases. These free iron phases form metallic iron upon subsequent reduction in hydrogen. Thermo gravimetric analysis (TGA) is used to quantify oxygen transport under alternating oxidizing/reducing conditions. TGA results indicate that at least 18% of all the iron, present in olivine, is capable of transferring oxygen on the time scale of minutes. X-ray photoelectron spectroscopy (XPS) combined with depth profiling provides insight in the dynamic behavior of olivine under relevant conditions. Iron enrichment at the surface is observed; oxidized olivine has an iron rich surface layer of 400 nm. The increased iron concentration is particularly pronounced at the outermost surface. Upon subsequent reduction, the iron quickly redistributes in the olivine toward the original, homogeneous distribution. These results show that oxygen transport should be taken into account when olivine is evaluated as a catalyst for indirect biomass gasification. Furthermore, both oxygen transport and catalytic properties are heavily dependent on the iron phases present in the material, which in turn depend on the gas environment.

1. Introduction

To meet the increasing demand for renewable, CO_2-neutral energy, biomass (in particular waste products) can be used for the production of such fuels as hydrogen, synthetic natural gas or Fischer–Tropsch diesel [1,2]. Conversion of biomass to fuels can be performed using the gasification process as an initial step in the conversion [3,4]. The resulting primary products CO, H_2, CO_2 and CH_4 can easily be used in the present infrastructure. Moreover, technology for converting CO and H_2 into conventional fuels, such as diesel, is already at hand [5].

The endothermic gasification process is sustained by allowing partial combustion of the biomass, usually using air. If the heat required for the endothermic gasification is not supplied by partial combustion in the gasifier section, but instead comes from a separate combustion step, which may be integrated in the gasification system, one speaks of indirect gasification. The main advantages of indirect gasification are the higher heating value of the produced gas, no N_2 contamination of the product gas and that a major part of the CO_2 produced in the process is separated from the product gases, allowing for sequestration.

In a typical indirect gasification system, a bed material is circulated between an oxidation reactor and a gasification reactor, coupled together. In the latter, biomass reacts with steam and is converted to a gas mixture consisting mainly of methane, synthesis gas and CO_2. The bed-material, together with the unconverted biomass fractions, tar and char, are fed into the oxidation reactor, to heat up the bed material. The hot bed material subsequently enters into the gasification zone to provide the heat, necessary for gasification. In addition to the main product gases, the gasification process always results in tar formation due to incomplete decomposition of the biomass. Tars decrease process efficiency and can cause fouling of downstream equipment. This constitutes a major obstacle in the way to large scale commercialization of the technique.

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Tar in the product gas can be decreased by using a reactive bed material [6–10]. A widely used and investigated bed material is the naturally occurring mineral olivine ($(Mg,Fe)_2SiO_4$) [11–14], in which iron is the catalytically active component for tar conversion [15–19]. Olivine is, however, not a stable material under process conditions, relevant for biomass gasification [14,20]. It has been shown that iron in olivine is highly mobile under alternating oxidizing and reducing environments [12]; iron enrichment at the surface is observed upon oxidation, whereas a decreased content is seen upon reduction [21]. Furthermore, the iron in olivine is oxidized in the oxidation zone and reduced in the gasification zone, and is thereby able to transport oxygen to the gasification zone. Oxygen transport lowers the necessary amount of steam for the gasification and increases tar degradation and fuel conversion [16,22], but it also (unwantedly) increases the CO_2 content in the gasification zone.

This work focuses on the role of iron in the chemical looping process. When olivine is used as a circulating bed material, it is sequentially exposed to different gas environments on time scales from a few seconds to several minutes. Changes in the gas environment influence the phase composition of olivine in general, and the surface concentration and oxidation state of iron in particular. The dynamics of these effects have not been well documented yet. With this paper, we aim at clarifying the time dependent changes in olivine (and especially the Fe-components contained therein) in rapidly changing, yet well-defined, chemical environments.

We have used Mössbauer spectroscopy to determine the distribution of different iron species in olivine after oxidation and reduction treatments. Furthermore, we present thermo gravimetric analysis (TGA) as a valuable characterization tool to quantify oxygen transport of olivine, since exact figures or relations to quantify the amount of this transported oxygen are unknown. To get detailed information on the dynamic behavior of iron at the surface and sub-surface layers under oxidizing and reducing conditions, we use X-ray photoelectron spectroscopy (XPS) combined with depth profiling.

2. Experimental

2.1. Catalyst material and treatments

For all experiments, natural olivine from Magnolithe GmbH was used. A 3 h, 1600 °C calcination in air was performed by the mineral supplier to improve its mechanical properties. The grain size during this pre-calcination was on the order of 10 mm. The composition of this olivine is well-known and extensively documented [7,12,13]. The iron content of our olivine sample was determined by ICP-AES to be 6.3 wt.%.

Prior to our experiments, the olivine was grinded to a powder with grain sizes of several micrometers, as estimated from scanning electron microscopy (SEM) images. The olivine powder has a specific surface area of $0.53\,m^2/g$ [23]. This grinded olivine will be denoted as "untreated" in this paper.

The grinded olivine powders were treated in a quartz tube flow reactor. Oxidation (20% O_2 in Ar) and reduction (pure H_2) treatments were applied at 750 °C. Total gas flows were set to 200 mL/min. In all experiments, the samples were first heated to 750 °C under pure Ar flow. At this temperature, the gas flow was switched to the reactive gas mixtures for a specified time. After treatment, the gas mixture was switched back to Ar and the reactor was quickly cooled to room temperature.

2.2. Mössbauer spectroscopy

Transmission ^{57}Fe Mössbauer spectra were collected at room temperature with a conventional constant-acceleration spectrometer using a ^{57}Co(Rh) source. Velocity calibration was carried out using an α-Fe foil. The Mössbauer spectra were fitted using the Mosswinn 3.0i program [24].

2.3. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) is a commonly used technique for studying reactive gas–solid systems. For measurements, the grinded, untreated olivine sample (200 mg) was placed in a porous quartz glass sample holder, connected by a platinum wire to a Sartorius 4406 balance, which measured the mass change of the sample during treatment. Gas treatments (oxidation (air, 8 mL/min) and reduction (30% H_2/N_2, 8 mL/min)) were applied at 750 °C in a home-built set-up, which is described in more detail elsewhere [25]. In between the oxidation and reduction treatment, the system was flushed with N_2 for 1 min to prevent direct contact between H_2 and O_2.

2.4. X-ray photoelectron spectroscopy

In this study, X-ray photoelectron spectroscopy (XPS) was combined with depth profiling. An ion gun was used to etch the sample's surface for a period of time before being turned off while XPS spectra were measured. Each etch step exposes a new surface and, by fitting the measured XPS spectra, the elemental concentrations at that specific surface could be determined. The objective of these experiments was to plot the trend in the atomic concentration values as a function of etch-time, or sample depth.

Olivine powder samples were supported on conductive carbon tape. XPS spectra were recorded using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα, 1486.6 eV) operating at 72 W and a spot size of 400 μm.

Region scans were measured at a constant pass energy of 50 eV. The background pressure was 2×10^{-9} mbar and during measurement 3×10^{-7} mbar argon, because of the charge compensation dual beam source.

Sputtering for depth profiling was done with an Ar^+ ion beam energy of 2000 eV at medium current (12 μA). The ion gun was used for 120 s for each etch step, corresponding to a total depth per etch level of 37.2 nm for a Ta_2O_5 reference.

Analysis and quantification of the measurements were performed using the CasaXPS software, using the Fe 3p, Mg 2p, Si 2p and O 1s regions.

3. Results

3.1. Mössbauer spectroscopy

Mössbauer spectroscopy was used to quantify the changes in the iron (oxidation) state of the olivine upon oxidizing and reducing treatments. The fitted spectra are presented in Fig. 1. The detailed fitting parameters and spectral contribution of the different iron species are presented in Table 1.

Fitting of the spectra in Fig. 1 required the use of two doublets and four sextuplets. The two doublets are attributed to Fe^{2+} in the olivine phase (D1) and Fe^{3+} in superparamagnetic hematite (D2), respectively [20]. Of the four sextuplets, the first two (S1 and S2) are identified as belonging to Fe^{3+} in octahedral and tetrahedral sites of the spinel structure of magnesioferrite ($MgFe_2O_4$) [12,26].