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The influence of iron oxide on the oxidation kinetics of synthetic char derived from thermogravimetric analysis and fixed-bed experiments under isothermal and temperature-programmed conditions

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ABSTRACT

The catalytic effect of iron oxide on the oxidation kinetics of synthetic char was investigated in a fixed-bed reactor and in a conventional thermobalance for comparison. Synthetic char doped with iron oxide was obtained by pyrolyzing hydrochar at 800 °C, which had been synthesized by hydrothermal carbonization of cellulose in the presence of iron oxide. Isothermal char oxidation in the fixed-bed reactor resulted in the most reliable kinetic results. According to model-free kinetic analysis of these experiments at 15% conversion, iron oxide decreased the activation energy of char oxidation from 149 kJ/mol to 133 kJ/mol. Modeling of the conversion-time curves was first performed by using the uniform reaction model and then improved by using a n -th order power law. In the temperature range of 440–490 °C a very good agreement with the experimental data was achieved using $n = 0.6$. Activation energies amounting to 149 kJ/mol and 134 kJ/mol were derived for the undoped and iron oxide-doped char, respectively, well in line with the model-free analysis.

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1. Introduction

The combustion of fossil fuels such as lignite still contributes to the current electricity supply, especially in Germany. In order to increase the efficiency of coal combustion chambers by predictive engineering, kinetic data are required for the numerical simulation of the combustion process. The composition of lignites depends on their origin. In addition to the varying content of water and volatiles, lignites contain mineral compounds differing in composition and content. They are supposed to affect the combustion behavior as several metal oxides catalyze the oxidation of carbonaceous materials [1–7]. One of the minerals present in lignite is Fe_2O_3 [8–10]. The evaluation of the catalytic effect of iron oxide on the oxidation of a lignite char requires comparing its oxidation kinetics with that of an undoped char. Such a mineral-free lignite-like carbon material can be synthesized by hydrothermal carbonization of cellulose [11]. The resulting solid fuel is comparable to chemically leached rhenish lignite in structure and oxidation behavior [11]. The natural incorporation of minerals is imitated by *in situ* doping with Fe_2O_3 during the hydrothermal carbonization process, which

leads to a higher degree of contact between the iron oxide particles and the hydrothermally carbonized cellulose compared with tight-contact physical mixtures of the corresponding solids obtained by milling [8]. By subsequent thermal treatment of the undoped and Fe_2O_3 -doped hydrochar under inert conditions, the volatile components are removed resulting in a porous, char-like carbon material.

Here, the catalytic influence of iron oxide on the oxidation behavior of synthetic char was investigated by temperature-programmed and isothermal experiments in a fixed-bed reactor under well-defined flow conditions as well as in a conventional thermobalance for comparison. The applied low heating rates and isothermal temperatures are not consistent with industrial applications, but enabled us to derive intrinsic kinetic data, because the oxidation experiments were performed under kinetic control in the absence of limitations by mass transport [12,13]. The temperature-programmed thermogravimetric experiments were evaluated according to the Kissinger-Akahira-Sunose method [14]. The isothermal fixed-bed experimental results were analyzed by the model-free Arrhenius method and also by model-based kinetic methods. For the model-based analysis, a first order power law rate expression according to the uniform reaction model [15] and a n -th order power law were used.

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2. Materials and methods

2.1. Materials

A mineral-free and a Fe₂O₃-doped synthetic char were synthesized according to Ref. [11] by hydrothermal carbonization of cellulose followed by thermal treatment under inert conditions. For the undoped hydrochar, 6 g α -cellulose (Sigma Aldrich) were dispersed in 30 mL de-ionized water within a PTFE inliner of a 50 mL stainless steel autoclave. The hydrochar doped *in situ* with 5 wt% Fe₂O₃ was produced by adding 150 mg of Fe₂O₃ (Sigma Aldrich, sieve fraction < 5 μ m) to 6 g cellulose. The autoclave was heated for 24 h in an oven with hot air ventilation to 200 °C corresponding to a water vapor pressure of around 16 bar. After cooling to room temperature, the suspension was filtered and washed with de-ionized water until a neutral pH was reached. The obtained solid was dried at 105 °C for 24 h. The dried hydrochars were thermally treated in 50 mL/min N₂ up to 800 °C with a heating rate of 5 K/min, holding the final temperature for 2 h. The obtained undoped and Fe₂O₃-containing chars were labeled as HTC and Fe/HTC, respectively.

2.2. Characterization of chars

Elemental analysis (C, H) was performed using an EURO EA 3000 Elemental Analyzer (HEKAtech). The iron content was obtained by atomic absorption spectroscopy (AAS) using a flame spectrometer (SpectraAA 220, Varian). N₂ physisorption measurements were performed in a BELSORP-max (BEL Japan), and the resulting isotherms were evaluated according to the Brunauer-Emmett-Teller (BET) method. Proximate analysis was conducted in a magnetic suspension balance (Rubotherm) according to the ASTM standard. The amount of volatile components was determined after increasing the temperature from room temperature to 900 °C by 10 K/min in flowing He (100 mL/min) taking into account the mass loss after 30 min at the final constant temperature. The remaining sample was cooled to 850 °C within 30 min and treated in a gas flow of 20 mL/min O₂ and 80 mL/min He recording the incombustible mass fraction as ash content.

2.3. Kinetic oxidation experiments

Oxidative thermogravimetric analysis (TGA) was performed in a magnetic suspension balance (Rubotherm) with a coupled on-line mass spectrometer (Pfeiffer, ThermoStar). For the TGA experiments, approximately 25 mg of the undiluted sample were heated at atmospheric pressure from room temperature to 900 °C with linear heating rates of 2, 5, 10 or 15 K/min at a constant flow rate of 100 mL/min 20% O₂ in He (99.995%/99.999%). The error of the thermogravimetric experiments was determined as ± 3 °C by repeated measurements.

Isothermal as well as temperature-programmed fixed-bed measurements were carried out in a continuous flow set-up at atmospheric pressure in synthetic air (20% O₂/Ar). A quartz tube reactor with an inner diameter of 8 mm was loaded with a fixed bed of 20 mg char (unsieved) diluted with 480 mg high purity SiC (sieve fraction 125–180 μ m). The product gas was analyzed continuously by a multi-channel analyzer (MLT4, Rosemount/Emerson) providing the mole fractions of CO, CO₂ and CH₄ by a non-dispersive IR-detector and of H₂ by a thermal conductivity detector. O₂ was detected by a paramagnetic O₂ analyzer (Magnos 16, Hartmann & Braun). Temperature-programmed oxidation (TPO) reactions were carried out with linear heating rates of 2, 5, 10 or 15 K/min in a flow of 20 mL/min 20% O₂ in Ar (99.995%/99.999%). For the isothermal oxidation experiments, the sample was first

heated to the reaction temperatures in the range of 450–490 °C (steps of 10 °C) for the undoped char and 440–480 °C for the iron-doped char by 10 K/min in 20 mL/min Ar. After the final temperature had been held for 15 min, the oxidation was performed in 20 mL/min 20% O₂ in Ar until no more oxygen consumption and CO_x formation was observed. The temperature uncertainty of measurements performed in the fixed-bed set-up amounted to ± 5 °C.

Temperature profiles along the fixed bed were determined by 4 thermocouples inserted into a ceramic tube (3 mm outer diameter) included in the radial center of the quartz tube reactor during the isothermal oxidation experiments of the undoped and doped char at 470 °C.

For the determination of kinetic parameters, the degree of conversion α was used, determined for the dynamic TGA experiments by

$$\alpha(T) = \frac{m_0 - m_T}{m_0 - m_{ash}}, \quad (1)$$

where m_0 is the initial mass of the synthetic char on a dry basis, m_T the measured mass at a certain temperature T and m_{ash} the final mass remaining after the thermogravimetric experiment.

For the fixed-bed experiments, the added mole fractions of CO and CO₂ (x_{CO_x}) produced until a certain time or temperature were related to the total amount of carbon oxides obtained by integration. The degrees of conversion of the temperature-programmed experiments were determined according to Eq. (2), and for the isothermal reactions by Eq. (3)

$$\alpha(T) = \frac{\int_0^T x_{CO_x} dT}{\int_0^\infty x_{CO_x} dT} \quad (2)$$

$$\alpha(t) = \frac{\int_0^t x_{CO_x} dt}{\int_0^\infty x_{CO_x} dt}. \quad (3)$$

The model-free determination of the apparent activation energy of the temperature-programmed experiments by the Kissinger-Akahira-Sunose method required the heating-rate dependent temperature T for a certain degree of conversion, which was calculated by the added effluent mole fractions of CO and CO₂. For the isothermal experiments, the activation energy was calculated at 15% conversion.

For the model-based analysis, the NETZSCH Thermokinetics software was used. Modeling was performed applying a first and n -th order power law rate expression giving also access to the apparent activation energy.

2.4. Kinetic analysis

For the kinetic analysis, the temperature and concentration dependence of the reaction rate was separated implementing the temperature dependence by the Arrhenius approach

$$r = A \cdot \exp\left(\frac{-E_A}{RT}\right) \cdot f(\alpha(t)). \quad (4)$$

The apparent activation energy E_A and the pre-exponential or frequency factor A are the kinetic parameters, R represents the universal gas constant and T the temperature.

Considering the kinetic parameters E_A and A as temperature-independent and assuming constant concentrations for a certain degree of conversion, the isoconversional Arrhenius activation energy of a n -th order power law is derived by

$$\ln r = \frac{-E_A}{R} \cdot \frac{1}{T} + \ln A'. \quad (5)$$

When plotting $\ln(r)$ as a function of the inverse temperature shows a linear relationship, the Arrhenius equation is valid, giving access to E_A and A' via the slope and interception, respectively.

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