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Research article

Investigation of NO conversion by different types of sewage sludge chars under low temperature

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ABSTRACT

Different types of sludge chars, i.e. the original (S1), HNO_3 washed (S2), KOH activated (S3), and H_2 reduced chars, were prepared to investigate their performances for NO conversion under low temperature. Results indicated that the surface area of the sludge chars did not play key role on NO conversion. S1 showed the higher NO conversion performance than S2 and S3, due to the reducing effect of iron components in S1 (mainly FeS and Fe_2P). Both H_2 reduction at high temperature and the followed cooling atmosphere (H_2 or N_2) have great influences on the activity of S1. H_2 reduction can promote the reducing capacity of the iron components, thus the performance of S1 for NO conversion was also significantly enhanced. However, NO conversion over S1 decreased in the presence of O_2, because the iron components were more quickly oxidized in O_2 atmosphere. Results of duration tests showed that the activity of S1 decreased with time, but it can be recovered by calcination in N_2. The profiles of the temperature programmed desorption (TPD) of CO and CO_2 indicated that CO and CO_2 emissions are mainly from the decomposition of oxygen functional groups (OFGs), including anhydrides, phenols, esters, and carboxylic acid. Furthermore, mechanisms of NO adsorption and conversion by S1–S3 were explored by an in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It was found that NO adsorbed on the sludge chars mainly transferred into NO_2 species at 50 °C, and then NO_2 species were gradually oxidized to nitrate species with the increase of temperature. Finally, the possible reaction routes for NO conversion were proposed based on experimental data.

1. Introduction

Sewage sludge production in China has been continuously increasing due to increased handing capacity of wastewater by stringent regulation of wastewater treatment (Deng et al., 2009). Nowadays, more than 40 million tons of sewage sludge are annually generated from municipal wastewater treatment plants in China (Gu, 2016). Sewage sludge pyrolysis is usually considered as an interesting energy alternative, and will lead to the production of char, oil, and gas (Kim and Parker, 2008). The sludge char is a solid residue with a porous structure, mainly composed of ash and carbon (Rozada et al., 2003). It has been widely reported that activated carbon can be produced from sludge char by physical or chemical activation, and shows high potential as an adsorbents for control of pollutants (Smith et al., 2009). On the other hand, since the sludge char is characterized by high ash content, metal components in the ash may act as active centers for some chemical reactions, which allows for in-situ conversions of some pollutants (Gu et al., 2012).

The main purpose of this study is to explore the potential application of sludge char in NO conversion. In fact, carbon based catalysts (such as nanotubes, activated carbons, carbon blacks and chars) have gained much attentions for NO conversion in recent years, since their advantages include low costs in synthesis, non-toxicity, easy transportation and handling (Wu et al., 2014). Two mechanisms are usually involved in NO conversions by carbon based materials, i.e. adsorption and catalyzation. In the early times, studies were mainly focused on adsorption properties of NO by carbon-based materials (Kong and Cha, 1996; Shirahama et al., 2002). In recent years, many attentions have been concentrated on NO conversions by loaded carbons, especially with transition metals (Illá-Gómez et al., 1999; Xue et al., 2008; Wang et al., 2017). For example, iron loaded in a carbon matrix has been considered as one of the most promising candidates (Busch et al., 2015; Li et al., 2016; Xiao et al., 2016). Illá-Gómez et al. (1999) reported that the catalytic effect of transition metals is evident by lowering the NO

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conversion temperature from 400 °C (for metal-free activated carbon) to 150–250 °C in the presence of metals. During NO-carbon reaction, it was considered that metals participate in a redox mechanism, where catalysts are oxidized by NO and reduced by carbon (Illá-Gómez et al., 1999). Since elevated temperature will lead to catalyzed gasification of carbon, lowering the working temperature is especially important for carbon-based catalysts (Busch et al., 2015).

Since sludge char is characterized by high ash content and low heating value, it is usually considered landfill material rather than an alternative fuel (Hwang et al., 2007). However, there are usually high content of metals in sewage sludge ash, especially the iron components which mainly originate from ferric flocculants introduced during wastewater treatment (Chai et al., 2014). As referred above, iron is one of the most promising transition metals for NO conversion, thus sludge char may be a potential catalyst for NO conversion. However, to the best of our knowledge, there is no public report on NO conversion catalyzed by the iron components in sludge char. Presently, only a few reports on NO conversion by sludge char can be found (Peng et al., 2008; Jo et al., 2011; Chen et al., 2015). In order to enhance the activity of sludge char, gaseous reducing agents like NH_3 and CO are often introduced. Jo et al. (2011) reported that sewage sludge chars activated chemically using KOH demonstrated higher de-NO_x performance than commercial activated carbon in the presence of NH_3. Additionally, 10–50% NO_x removal (at 250–300 °C) by chars produced from sewage sludge pyrolysis has also been reported, and KOH activation is considered as a competitive option for enhancing NO_x conversion (Chen et al., 2015). Peng et al. (2008) found that sludge char showed high efficiency for selective catalytic reduction of NO by CO, the maximum conversion of NO can reach 97.1% at 450 °C. Although gaseous reducing agents can effectively improve NO conversion performance, there are still some disadvantages associated with the use of them. For example, NH_3 is an expensive agent with disadvantages including toxicity, corrosion, and byproducts, etc. Therefore, it will be much meaningful for catalysts to sustain high performance in the absence of gaseous reducing agents. It has been reported that the activity of carbon can be greatly improved by oxidation in HNO_3 or H_2O_2 solution (Xue et al., 2008). Bhaduri and Verma (2015) reported that carbon materials doped with Cu can achieve a high activity for NO conversion without requiring additional reducing agents.

In this study, sludge chars were prepared and pretreated by washing with HNO_3, activation with KOH or reduction with H_2. NO conversions by different sludge chars were investigated and compared without introducing additional reducing agents. The sludge used in this study was characterized by high content of iron, thus special attentions were paid to the effect of iron on NO conversion. Formation mechanisms of CO and CO_2 during NO conversion were analyzed, and NO adsorption and conversion mechanisms over the sludge chars were also detailed explored by DRIFTS technique.

2. Materials and methods

2.1. Materials

A kind of mechanically dewatered sewage sludge with moisture content of 83.1 wt% was sampled from a municipal wastewater treatment plant in Shanghai, China. The wet sludge sample was dried in an electric drying cabinet at 105 °C for 12 h. Three kinds of sludge chars, i.e. the original char (S1), the acid washed char (S2) and the activated char (S3), were prepared from the dried sludge. S1 was produced from pyrolysis of the dried sludge in N_2 atmosphere at 800 °C for 30 min. S2 was produced by acid washing of S1 in HNO_3 solution (20 wt% concentration) at 80 °C for 2 h, followed by rinsing with distilled water, and finally dried at 105 °C for 12 h. S3 was produced by calcination of KOH/S1 mixtures (uniformly mixed with KOH/S1 mass ratio of 1/3) in N_2 atmosphere at 700 °C for 1 h, followed by washing with 5.0 M HNO_3 and distilled water, and finally dried at 105 °C for 12 h.

H_2 reduced sludge chars were also prepared to investigate their performances for NO conversion. H_2 reduction pretreatment of S1–S3 were conducted in a quartz tube reactor with a 12 mm inner diameter. In the procedure, 1.5 g of sludge char was placed in the reactor, and H_2–N_2 mixtures (5 vol% of H_2) were introduced into the system with total flow rate of 60 mL/min. The reactor was electrically heated from room temperature to 800 °C at a rate of 5 °C/min, where it was held for 1 h before cooling to room temperature in a N_2 (labeled as HRN) or in a H_2–N_2 mixture atmosphere (5 vol% of H_2, labeled as HRH). Table 1 shows the sludge chars prepared for NO conversion tests.

2.2. NO conversion tests

NO conversion tests were carried out in the quartz tube reactor under atmospheric pressure. In the test, 1.5 g of sludge char was placed in the tube and fixed by silica wool. Reactant gas was prepared by mixing pure N_2 with NO. The volume fraction of NO was 0.08 vol% in each experiment. The flow rates of N_2 and NO were respectively controlled by two mass flow meters, and the total flow rate was controlled at 1.0 L/min, corresponding to a gas hourly space velocity (GHSV) of 33970 h^{-1}. Initially, the reactant gas was continuously fed into the reactor, and the effluent gas species, including CO, CO_2, NO and NO_2, were measured using an online gas analyzer (Testo-350L, Germany). N_2O was analyzed by an online Gas Chromatography (GC) with a thermal conductivity detector (TCD) (Porapak-Q chromatographic column).

When outlet NO concentration was stable (i.e. sludge char was in saturated NO adsorption state), the reactor was electrically heated at a rate of 5 °C/min to 500 °C. NO conversion was calculated as follows:

$$\text{NO conversion}(\%) = \left(1 - \frac{[NO]_{out}}{[NO]_{in}}\right) \times 100\% \quad \text{(R1)}$$

where $[NO]_{out}$ and $[NO]_{in}$ are the NO concentrations at the outlet and inlet of the reactor, respectively.

2.3. Characterization of the materials

The proximate and ultimate analyses of the chars were determined in a thermo-balance (SDLA618) and in an elemental analyzer (Varo EL III), respectively. An inductively coupled plasma emission spectrometer (ICP-AES, Leeman Prodigy) were used for P and metal elements analyses in the chars. The N_2 adsorption-desorption isotherms were measured in a Micromeritics Tristar 3020 apparatus. Based on the isotherms data, the specific surface area of the

Table 1
Sewage sludge chars prepared for experiments.

Samples	Preparing methods	Cooling atmosphere after H_2 reduction
S1	Pyrolysis of sewage sludge	/
S2	Acid washing of S1	/
S3	Activation of S1	/
S1-HRN	H_2 reduction of S1	N_2
S2-HRN	H_2 reduction of S2	N_2
S3-HRN	H_2 reduction of S3	N_2
S1-HRH	H_2 reduction of S1	5 vol% H_2 + 95 vol% N_2