Fuel 191 (2017) 511–517

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

CrO_3 supported on sargassum-based activated carbon as low temperature catalysts for the selective catalytic reduction of NO with NH_3

Sujing Li, Xiaoxiang Wang, Shan Tan, Yun Shi, Wei Li *

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology and Environment, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

A R T I C L E   I N F O

Article history:
Received 18 April 2016
Received in revised form 22 November 2016
Accepted 24 November 2016
Available online 5 December 2016

Keywords:
Sargassum-based activated carbon
Chromium
Low temperature NH_3-SCR
Water and sulfur tolerance

A B S T R A C T

Sargassum based activated carbon (SAC) doped with various transition metals was developed via impregnation as a new catalyst for selective catalytic reduction of NO with NH_3 (NH_3-SCR) in the temperature range of 50–250 °C with gas hourly space velocity (GHSV) of 80,000 h^{-1}. The samples were characterized by means of Brunauer–Emmett–Teller method (BET), scanning electron microscope (SEM), NH_3 temperature-programmed desorption (NH_3-TPD), H_2 temperature-programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS). The impacts of water (H_2O) and sulfur dioxide (SO_2) on the SCR activity of the CrO_3/SAC catalyst were also discussed. The experimental results showed that the introduction of Cr increased the acid sites formed on the surface of catalysts and enhanced the SCR reaction rate by the valence changing between Cr^{6+} and its lower oxidized states (Cr^{5+}, Cr^{3+} and Cr^{2+}). The catalyst with a Cr/SAC mass ratio of 2%:1 exhibited the best NO_x-removing performance, with NO_x conversion greater than 90% at the temperature of 125–150 °C. Moreover, it had excellent water and sulfur tolerance, making the Cr-doped SAC catalyst as a good candidate for reducing the NO_x emission from fired power plants.

1. Introduction

Selective catalytic reduction with ammonia (NH_3-SCR) is an efficient and economic technique for the abatement of NO_x from exhaust gases of coal-fired power plants [1]. Currently, V_2O_5-WO_3 (MoO_3)/TiO_2 is the most widely applied catalyst with a narrow temperature window of 300–400 °C [2–4]. However, the SCR unit is normally suggested to be located behind particulate collector (ESP) and desulfurization (FGD) equipment in power plants, where the flue gas temperature could drop to 50–60 °C [5]. To achieve the desired working temperature (normally 350–500 °C) for the V-based catalysts, reheating the flue gas is required, resulting in the significant energy consumption. In addition, low N_2 selectivity as a result of formation of N_2O, high conversion of SO_2 to SO_3 [6,7], the toxicity of V_2O_5 to the environment, and the adverse effects of vanadium on human health are the urgent problems that need to be addressed. Consequently, to save energy consumption and be eco-friendly, developing new catalysts that would keep high activities under low temperature has become imperative and has attracted a lot of attentions [8,9].

Carbon materials are regarded as promising candidates for low temperature SCR catalysts. In addition, transition metal oxides (Ce, Mn and Cr) supported on carbon materials have shown an excellent catalytic performance and SO_2 resistance [10–13]. In our previous studies [14], sargassum-based activated carbon (SAC) was proved to be a good carbon-based material with high nitrogen content and rich surface functional groups, demonstrating to be a suitable support for SCR catalysts. Also, nitrogen modified sargassum-based activated carbon exhibited an excellent SCR activity with a maximum NO_x conversion of 87% at 150 °C. The utilization of sargassum-based activated carbon as a SCR catalyst support is an effective approach of combining waste disposal, biomass energy recovery and air pollution control in one process. However, it is necessary to increase the maximum NO_x conversion at lower temperature with higher GHSV by different modification methods, for further reducing the energy consumption on reheating the flue gas. In this work, various metals had been doped on the SAC to further improve its catalytic performance at low temperature.

Various chromium oxide loadings over catalysts as a promoter can lead to an increase in SCR activity [15]. The NO_x removal rate

---

* Corresponding author.
E-mail address: w_li@zju.edu.cn (W. Li).

http://dx.doi.org/10.1016/j.fuel.2016.11.095
0016-2361/

for a series of alumina-supported CrO_3 and Fe_2O_3 catalysts prepared by Gorge et al. increased by 10% with the addition of small amounts of Cr [16]. Chen et al. reported that addition of Cr into the MnO_x lattice was the crucial factor to enhance the SCR activity over the Cr-Mn catalysts [17]. Donovan et al. also found that titanium-supported Mn, Cr and Cu performed well at low temperature due to the increase of acid sites on the surface [18]. Pasel et al. found that the loading of transition-metal oxide (Fe_2O_3, Cr_2O_3 and CuO) on the commercial active carbons led to an increase in SCR activity [15]. Chromium was used as a promoter to improve the performance of Pt/ZSM-35 by Yu et al. and an increase of NO conversion from 80.5% to 94.7% was obtained at 120 °C [19]. They found that Cr addition not only enhanced the adsorption of NO_x but also promoted the formation of surface NH^{4+} species. Although chromium was often applied as a promoter for metal oxides, seldom literature investigated its enhancing effect on the carbon supports during SCR and the optimum content of Cr doping was rarely studied.

In the present study, various metals (Mn, Cr, Ce) were selected as the active components to improve the catalytic performance of sargassum-based activated carbon catalyst and the effect of different Cr doping amounts on the SCR activity of SAC catalyst was also studied. Moreover, a series of analytical techniques, including SEM, BET, XPS, NH_3-TPD and H_2-TPR, were employed to get insight into the enhancing role of Cr. In addition, the impacts of SO_2 and H_2O on NH_3-SCR activity over metal-modified catalysts were investigated.

2. Experimental

2.1. Catalyst preparation

The activated carbon was prepared using a mixture of H_3PO_4 and air-dried sargassum with a mass ratio of 2:1 in a tubular quartz reactor, which was described in detail in our previous publication [14]. The precursor was activated by being heated up to 500 °C with a heating rate of 10 °C/min for 1 h under a stream of nitrogen (400 mL/min). Then, the sample was cooled down to room temperature. The resulted activated carbon was washed with 1 mol/L HCl solution, followed by deionized water. It was dried and sieved to obtain a particle size range of 40–60 mesh, named as SAC.

Metal modified catalyst was prepared by impregnating SAC with various metal salt solution ($C_4H_6MnO_4{\cdot}4H_2O$, $CeSO_4{\cdot}4H_2O$, CrO_3). The slurry was mixed via sonication for 2 h and then held at ambient temperature for 12 h. Afterwards, the impregnated samples were heated under a stream of nitrogen up to 500 °C for 1 h before cooled down to room temperature. The metal modified catalysts were denoted as M(x)/SAC, where M stood for the metal, including Mn, Ce, Cr while x represented the different mass ratio of Metal/SAC. For the SAC and Metal/SAC, they are both based on sargassum. The proximate and ultimate analyses were carried out on the sargassum, as shown in Table 1.

2.2. Catalytic activity test

NH_3-SCR activity of the catalyst was tested in a fixed-bed quartz tube reactor, which was described in detail in our previous study [14]. The reaction conditions were set as following: 0.10 g catalyst, 500 ppm NO, 500 ppm NH_3, 5v/v% O_2, 100 ppm or 300 ppm SO_2 (when used), 5% or 10% H_2O (when used), N_2 as carrier gas with a GHSV of 80,000 h^{-1}. Water vapor was generated by passing N_2 through a heated bottle containing deionized water. Prior to catalytic tests, the catalysts were heated up to 500 °C for 30 min under N_2 to purify the sample surface. The reactor was then cooled down to 30 °C and N_2 was switched to reaction gas mixture. For each experiment, fresh samples were used and their catalytic activities were estimated within the temperature range of 50–250 °C under steady-state conditions.

The outlet concentration of reactants and products were continuously monitored by a Nicolet iS50 FTIR spectrometer coupled with a heated FTIR gas cell. The NO_x conversion and N_2 selectivity were obtained by using the following Eqs. (1)–(3):

$$NO_x\ \text{conversion} = \frac{C_{NO_x(in)} - C_{NO_x(out)}}{C_{NO_x(in)}} \times 100\% \tag{1}$$

$$C_{NO_x} = C_{NO} + C_{NO_2} + 2C_{N_2O} \tag{2}$$

$$N_2\ \text{selectivity} = \left(1 - \frac{2 \times C_{N_2O}}{C_{NO_x(in)} + C_{NH_3(in)} - C_{NO(out)} - C_{NO_2(out)} - C_{NH_3(out)}}\right) \times 100\% \tag{3}$$

2.3. Catalyst characterization

The morphologies of Cr/SAC catalysts with different chromium doping contents were studied by using scanning electron microscopy (philips model FEI model Quanta 400 SEM).

Nitrogen adsorption isotherms were measured at liquid nitrogen temperature (77 K) using a Quantachrome Autosorb-1C apparatus. The specific surface area was calculated by using the BET method. The total pore volume and micropore surface area were calculated using the t-plot method.

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo ESCALAB 250 electron spectrometer equipped with an Al-$K\alpha$ X-ray source (hv = 1486.6 eV). The XPS spectra were calibrated by taking the graphitic peak as 284.6 eV. Peak analysis was performed using Casa-XPS Version 2.1.9 software with all spectra Shirley-background subtracted prior to fitting.

NH_3-TPD was performed using quadrupole mass spectrometer to record the signals of NH_3 and NO_x. Prior to the TPD experiments, the samples (50 mg) were pretreated at 400 °C in a flow of He (30 mL/min) for 30 min and cooled down to 80 °C. Then the samples were exposed to a flow of NH_3 for 2 h, followed by Ar purging for 1 h. Finally, the temperature was raised to 1000 °C in a He flow at a rate of 10 °C/min. Prior to the H_2-TPR experiments, 50 mg samples were pretreated at 400 °C in a flow of He for 30 min and cooled down to 50 °C. The temperature was then raised to 1000 °C at a rate of 10 °C/min in a flow of H_2/Ar (30 mL/min).

3. Results and discussion

3.1. Effect of different doping metals on the NH_3-SCR activity of the catalysts

Different species (Mn, Ce, Cr) and loading amount of transitional metal were employed to seek out the catalyst with the highest NO_x conversion in the temperature range of 50–250 °C. With the introduction of metal species, a promotional effect is observed

Table 1
Proximate analysis and ultimate analysis of raw sargassum (wt%. dry basis) [14].

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%)			
	Water	Ash	Volatiles	Fixed carbon	C	H	N	O
Sargassum	6.7	6.6	54.7	32	40.3	5.4	2.5	51.8