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Featured Letter

Heterogeneous Fenton oxidation of nitric oxide by magnetite: Kinetics and mechanism

Siyuan Yang [a], Yuanquan Xiong [a,*], Yangyang Ge [a], Shuping Zhang [b]

[a] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, Jiangsu, China
[b] School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT

Magnetite materials were used for catalytic decomposition of peroxide hydrogen since Fe^{2+} can react with peroxide hydrogen directly to generate **.***OH* rather than Fenton-like reaction. The purpose was to determine the NO oxidation under various working conditions. The features of fresh and used catalysts was analyzed according to XRD and XPS. In addition, the reaction conform to a pseudo-first order kinetics pattern on the basis of results. The rate constants was calculated by different results and the activation energy for the reaction was obtained as 32.07 kJ/mol.

1. Introduction

Nitrogen oxides (NOx) emitted from coal-fired power plants have caused significant environmental issues, such as ozone layer depletion, photochemical smog and global warming [1,2]. Meanwhile, the NO accounts for more than 90% NOx in flue gas and it cannot be removed by scrubbing because of its' insoluble. Fenton process is a kind of strong oxidation system among Advanced oxidation processes (AOPs) and has been widely put into use in the water-treatment [3]. This process is known as the reaction between H_2O_2 and catalysts to generate highly active radicals, mainly low-selective **.**OH radicals with high oxidation potential. Magnetite is generally used in heterogeneous Fenton reaction. Little published information about magnetite as catalyst for advanced oxidation processes in fuel gas clean technologies. Therefore, the main objective of this research is to design a novel system to remove NO by heterogeneous Fenton with low H_2O_2 consumption.

2. Experimental section

2.1. Experimental process

The gas flow including N_2, NO and O_2 was controlled by mass flowmeter and the simulated flue gas blended completely in the buffer. Then H_2O_2 was injected into the fixed bed to achieve •OH radicals by decomposition of H_2O_2 on magnetite. The total flue gas flow rate was 1.5 L/min and the feeding rate of H_2O_2 was 5 mL/h, the oxygen content was 7 vol% and NO concentration is 500 ppm.

2.2. Preparation of catalyst

Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and ethylene glycol ($C_6H_{12}O_2$) in analytical grade was purchased from Sinopharm Chemical Reagent. Predetermined amount of 0.2 mol $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 100 mL $C_6H_{12}O_2$ and then stirred in a magnetic stirrer at 40 °C for 2 h. Gel was formed when solution heated at 80 °C for 2 h. The gel was then dried at 150 °C in an oven for 20 h. After that, the aerogel was mashed and calcined in N_2 at 400 °C for 2 h.

3. Results and discussion

3.1. Characterization

The XRD analysis of the catalysts was shown in Fig. 1. The different diffraction peaks at $2\theta = 18.4°$, 30.23°, 35.58°, 43.22°, 53.62°, 57.13° and 62.71° are corresponding to (111), (220), (311), (400), (422), (511) and (44 0) planes of magnetite, respectively. It was clear that only the phase of Fe_3O_4 was detected and there was no other phase such as α-Fe_2O_3 and γ-Fe_2O_3. In addition,

* Corresponding author.
E-mail address: yqxiong@seu.edu.cn (Y. Xiong).

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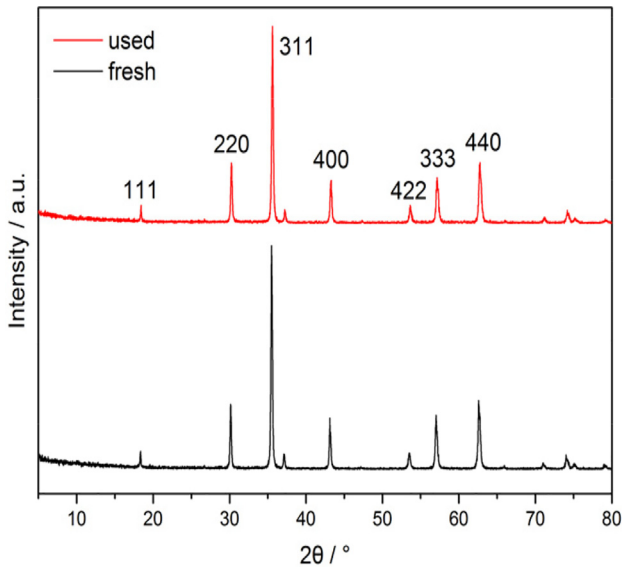

Fig. 1. XRD patterns of fresh and used catalysts.

crystalline phases of catalyst did not change significantly after reaction.

During this study, the Fe 2p XPS spectrum of fresh and used Fe_3O_4 was analyzed by the Shirley background-subtracted in Fig. 2. This spectrum indicated that iron comprised two oxidation states, Fe^{2+} and Fe^{3+}, which have been labelled on the spectrum. In the 2p3/2 region, the spectrum can be successfully fit to three main peaks and one satellite peak. As shown in Fig. 2a, the lowest binding energy peak at 709.54 eV was attributed to Fe^{2+}, with a corresponding satellite at 718.41 eV. The Fe^{3+} octahedral species was found with a binding energy of 710.59 eV and the Fe^{3+} tetrahedral species had a binding energy of 711.69 eV. The Fe^{3+} transform into to Fe^{2+} in the octahedral structure after reaction, which confirmed Eqs. (6) and (7). Fig. 2(c) and (d) also showed the O 1s spectra could be fit to three main peaks corresponding to about 530, 531 and 533 eV. The most obvious peak at 530.0 eV in both fresh and used sample due to lattice oxygen in Fe_3O_4, and two other peaks result from mono and bidentate carboxylate oxygen atoms.

3.2. Reaction order

The reaction time and concentration of NO depends exponentially in Fig. 3. According to the empirical kinetic model of NO oxidation, the overall oxidation rate could be described as follow [4,5].

$$r_{total,NO} = -\frac{d\langle NO\rangle}{dt} = k_1\langle \cdot OH\rangle + k_2\langle H_2O_2\rangle \quad (1)$$

where $r_{total,NO}$ represents the overall pseudo-first-order rate constant of NO oxidation; $\langle \cdot OH\rangle$ and H_2O_2 are the concentrations of $\cdot OH$ and H_2O_2, mol/L; $\langle NO\rangle$ is the concentration of NO at any time, ppm.

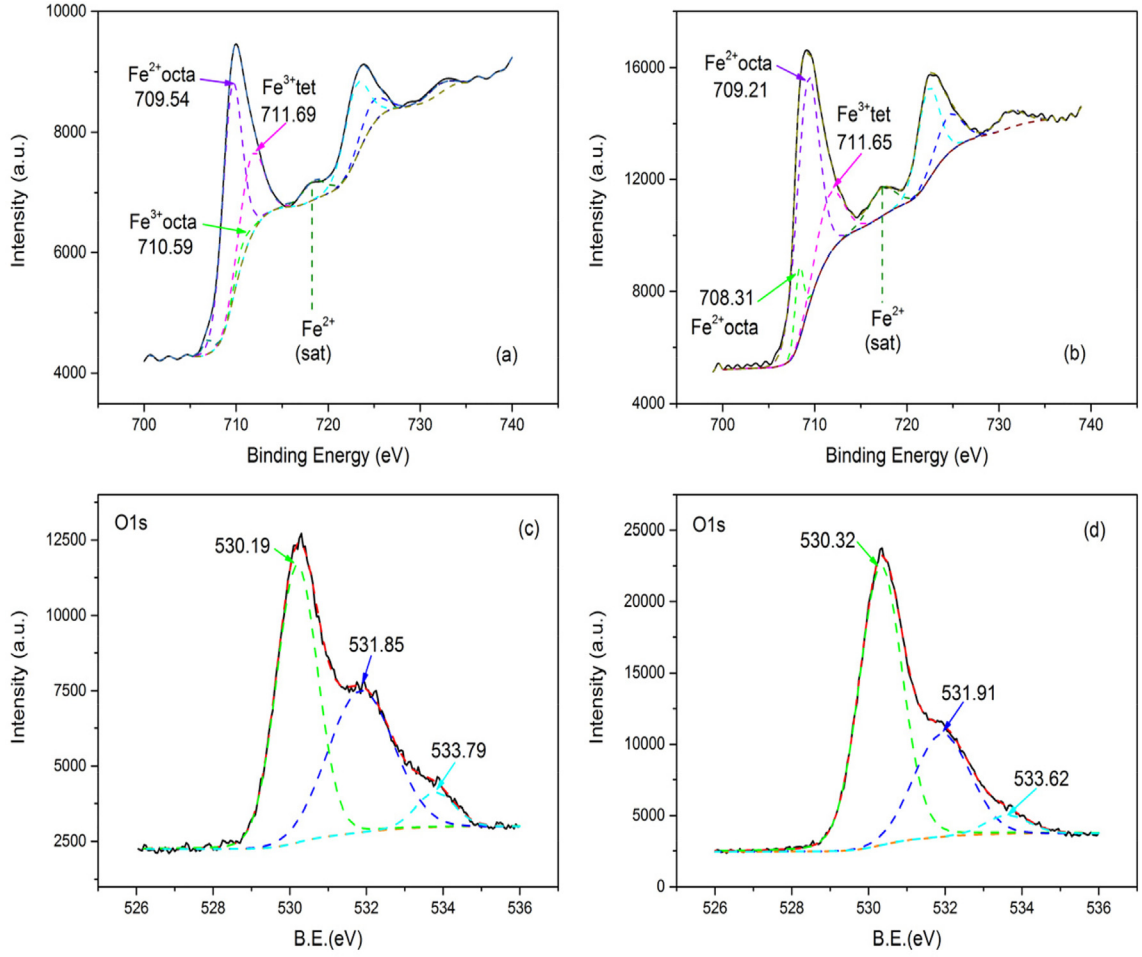

Fig. 2. Fe 2p spectra for fresh (a) and used (b) samples, O 1s XPS spectrum for fresh (c) and used (d) samples.