



Full Length Article

Low temperature selective catalytic reduction of NO_x with NH₃ by activated coke loaded with Fe_xCo_yCe_zO_m: The enhanced activity, mechanism and kinetics



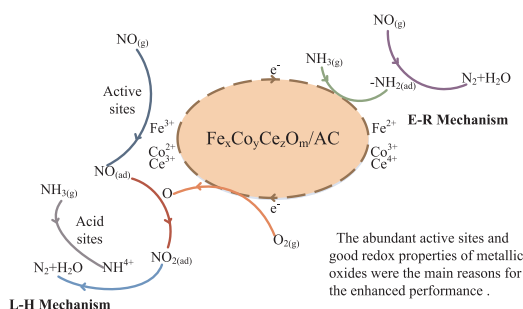
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GRAPHICAL ABSTRACT



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ABSTRACT

The existing catalysts based on activated coke had generally poor denitration performance at low temperature, which could not meet the urgent needs of power plants and steel enterprises. In this study, activated coke loaded with Fe_xCo_yCe_zO_m was prepared by incipient wetness impregnation method and employed to remove NO_x at 100–350 °C in simulated flue gas. 3%Fe_{0.6}Co_{0.2}Ce_{0.2}O_{1.57}/AC catalyst exhibited highest NO_x removal efficiency as it had more than 70%NO_x conversion rate at 100 °C and achieved more than 90%denitration efficiency at 250–350 °C. The catalyst also showed stable catalytic performance and good resistance to H₂O or/and SO₂ at 250 °C. Based on the results of Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), temperature programmed desorption (TPD), temperature programmed reduction (TPR) and Fourier transform infrared spectroscopy (FTIR), the enhanced performance could be attributed to the co-participation of Fe, Co and Ce species with different valence states, the high concentration of chemisorbed oxygen, highly dispersed active components, the increase of weak acid sites, good redox properties of metallic oxides and abundant functional groups on the catalysts surface. Finally, the possible mechanism and kinetics of NO_x removal over Fe_xCo_yCe_zO_m/AC catalyst were discussed in detail, which revealed that the enhanced performance was resulted from the increased active sites and the redox cycle among Fe, Co and Ce.

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1. Introduction

Nitrogen oxides (NO_x) is one of the main air pollutants, which could pose acid rain, photochemical smog and do harm to human health [1–3]. Since the gradual stringent standard for the concentration of air pollutants emissions, NO_x emissions has been decreasing year by year, but the total amount is still enormous [4]. Therefore, NO_x emission control continues to be a necessary aspect of air pollution control. Selective catalytic reduction (SCR) with ammonia is the most widely used technology in stationary sources with economic and technological efficiency taken into accounts [5–7]. For NH₃-SCR system, catalysts are the key part. Among numerous catalysts for NO_x removal, V₂O₅-WO₃(MoO₃)/TiO₂ is most widely useful commercial catalyst in coal-fired power plants as they have high denitrification efficiency [8]. But their drawbacks, such as narrow operation temperature window (300–400 °C), the toxicity of V₂O₅, low N₂ selectivity at high temperature, high costs and etc., constrained the application in industrial fields [9–11]. Therefore, it is imperative to develop nontoxic catalysts which have low costs, stability, high deNO_x activity at wide temperature range and favorable tolerance of other components in the flue gas.

Activated coke is a kind of porous carbon material which has not been fully activated [12]. Compared with activated carbon, it has similar pore structure, lower costs and higher mechanical strength [13]. Thus, activated coke has been used for flue gas desulfurization and is regarded as one of the promising materials for NH₃-SCR catalysts, which has attracted a lot of attention [14,15]. The existing catalysts based on activated coke had generally poor denitration performance at low temperature, which could not meet the urgent need of power plants and steel enterprises, so it is required to improve the efficiency of activated coke by modification and explore the mechanism of the enhanced ability.

A lot of efforts have been made in the modification of activated coke by doping with different kinds of metal oxides. Transition metal oxides, such as Fe₂O₃, Co₃O₄ and CrO₃, were proved to have the ability to improve deNO_x performance in the low- and medium-temperature range due to their various states and redox properties [16–18]. Iron oxides is nontoxic, abundant and low-priced, which has been used as one of main active components in the preparation of SCR catalysts [19,20]. It was reported that Fe_{0.3}Mn_{0.5}Zr_{0.2} catalyst prepared by coprecipitation method achieved excellent denitration performance and the NO_x conversion rate was up to 100% at 200–360 °C [21]. It also has good stability and strong resistance of SO₂ [21]. Anna Stahl et al. studied that Fe-W-Ce Mixed Oxide could exhibit excellent SCR activity and high resistance of SO₂ and/or H₂O because of the synergistic inhibition effect among Fe, Ce and W species and highly dispersed iron compounds [22]. Other iron oxides catalysts, like Fe_{0.7}Mn_{0.15}Mg_{0.15}O₂, Fe/Cu-SAPO-34 and Fe-Nb composite oxides, were deeply investigated [23–25]. Oxide of Cobalt has been reported that it could enhanced the SCR activity of catalysts because of its oxidation and adsorptive abilities [26]. Co₃O₄ was also reported that it was the active sites of sulfur dioxide which helped improve the resistance ability of sulfur dioxide for catalysts [27]. Gao et al. prepared MnCo₂O₄ microspheres and found it

had remarkable low-temperature catalytic activity, high N₂ selectivity in a wide temperature window and excellent water resistance [28]. Mn_{0.1}/Co_{0.3}-Ce_{0.35}-Zr_{0.35}O₂ showed excellent efficiency of NO_x reduction [29]. Furthermore, Different rare earth oxides, including La₂O₃, Nd₂O₃, Pr₆O₁₁ and CeO₂, were loaded onto activated semi-coke and Wang et al. reported that CeO₂/ASC had highest denitration rate, which was 78% at 300 °C [30]. Activated coke modified by MnO_x or/and CeO_x was prepared by Fu et al., which had achieved good denitration performance and its stability increased over time [31]. Cerium oxides has been widely used to remove NO_x because the shifts between Ce³⁺ and Ce⁴⁺ plays an important role in NO oxidation in favor of the fast SCR reaction [32]. Meanwhile, it has been proved that the addition of CeO₂ does good to improve the dispersion of other active components [2,33]. Given the above consideration, the combination of Fe, Co and Ce doped into activated coke might promise a SCR catalyst with excellent catalytic performance at low temperature, low costs and good resistance to SO₂ or/and H₂O. Meanwhile, there has been few reports on the facilitation effect of Fe_xCo_yCe_zO_m on activated coke to the best our knowledge.

In this paper, a series of Fe_xCo_yCe_zO_m was loaded on the activated coke (referred as AC) by incipient wetness impregnation method and were employed to remove NO_x at low temperature. The catalytic performance, lifetime and the effect of sulfur dioxide or/and water vapour were evaluated at a fixed-bed reactor in stimulated flue gas to produce a effective denitration catalyst. Moreover, the physicochemical properties of the catalysts were studied by various characterization methods, such as BET, XPS, XRD, NH₃-TPD, H₂-TPR and FTIR. Finally, the possible mechanism and kinetics of NO_x removal over Fe_xCo_yCe_zO_m/AC catalyst were discussed.

2. Experimental

2.1. Materials preparation

The AC, purchased from Shanxi Xinhua Chem.Co.LTD, China, was firstly washed in deionized water to remove the adhesive substance on the surface and then placed in a drying oven for 6 h at 105 °C. The cleaned AC was crushed and sieved into 20–40 mesh particles before modification. Other reagents used in this study, such as ferric nitrate (Fe(NO₃)₃·9H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O) and cerium nitrate (Ce(NO₃)₃·6H₂O), were purchased from Tianjin Fuchen Chemical Reagent Factory, Beijing Chemical Plant and Sinopharm Chemical Reagent Co. Ltd. as analytically pure (AR) reagents. What's more, modified AC was prepared by incipient wetness impregnation method.

The process of loading Fe₂O₃, Co₃O₄ and CeO₂ on the activated coke was as following: 10 g AC was dipped into the aqueous solution (25 mL) for 8 h at ambient temperature (about 30 °C), which was prepared according to Table 1. Then the sample was dried for 6 h at 105 °C in a drying oven. After drying, the sample was calcined for 4 h at 400 °C in tubular furnace with the heating rate of 10 °C/min under N₂ atmosphere. Finally, the sample was cooled down to room temperature with the protection of N₂. The activated coke modified by metallic oxides

Table 1
The dosage of agents in the material preparation.

Sample	m _{AC} /g	m _{Fe(NO₃)₃·9H₂O} /g	m _{Co(NO₃)₂·6H₂O} /g	m _{Ce(NO₃)₃·6H₂O} /g
1%Fe _{0.5} Co _{0.2} Ce _{0.3} O _{1.63} /AC	10	0.19	0.06	0.12
3%Fe _{0.5} Co _{0.2} Ce _{0.3} O _{1.63} /AC		0.56	0.18	0.36
5%Fe _{0.5} Co _{0.2} Ce _{0.3} O _{1.63} /AC		0.95	0.30	0.60
7%Fe _{0.5} Co _{0.2} Ce _{0.3} O _{1.63} /AC		1.33	0.42	0.84
9%Fe _{0.5} Co _{0.2} Ce _{0.3} O _{1.63} /AC		1.71	0.54	1.08
3%Fe _{0.3} Co _{0.2} Ce _{0.5} O _{1.72} /AC		0.3	0.14	0.53
3%Fe _{0.4} Co _{0.2} Ce _{0.4} O _{1.67} /AC		0.43	0.13	0.46
3%Fe _{0.6} Co _{0.2} Ce _{0.2} O _{1.57} /AC		0.76	0.18	0.27
3%Fe _{0.7} Co _{0.2} Ce _{0.1} O _{1.52} /AC		0.98	0.2	0.15

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