JOURNAL OF ENVIRONMENTAL SCIENCES 47 (2016) 100–108

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JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

# Regeneration of commercial selective catalyst reduction catalysts deactivated by Pb and other inorganic elements

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ARTICLE INFO

*Article history:*
Received 8 October 2015
Revised 22 December 2015
Accepted 22 December 2015
Available online 22 April 2016

*Keywords:*
Regeneration
SCR catalysts
Brønsted acid sites
Reducibility
Pb

ABSTRACT

The regeneration of commercial SCR (Selective Catalyst Reduction) catalysts deactivated by Pb and other elements was studied. The deactivated catalyst samples were prepared by chemical impregnation with mixed solution containing $K_2SO_4$, $Na_2SO_4$, $CaSO_4$, $Pb(NO_3)_2$ and $NH_4H_2PO_4$. A novel method combining Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and $H_2SO_4$ solution (*viz.* catalysts treated by dilute EDTA-2Na and $H_2SO_4$ solution in sequence) was used to recover the activity of deactivated samples, and the effect was compared with single $H_2SO_4$, oxalic acid, acetic acid, EDTA or $HNO_3$ solutions. The surface structure, acidity and reducibility of samples were characterized by $N_2$ adsorption–desorption, inductively coupled plasma optical emission spectrometer (ICP-OES), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), $H_2$-temperature programmed section ($H_2$-TPR), $NH_3$-temperature programmed desorption ($NH_3$-TPD) and *in situ* DRIFTS. Impurities caused a decrease of specific surface area and surface reducibility, as well as Brønsted acid sites, and therefore led to severe deactivation of the SCR catalyst. The use of an acid solution alone possibly eliminated the impurities on the deactivated catalyst to some extent, and also increased the specific surface area and Brønsted acid sites and promoted the surface reducibility, thus recovered the activity partially. The combination of EDTA-2Na and $H_2SO_4$ could remove most of the impurities and improve the activity significantly. The removal of Pb should be an important factor for regeneration. Due to a high removal rate for Pb and other impurities, the combination of EDTA-2Na and $H_2SO_4$ solutions provided the best efficiency.



## Introduction

Catalysts are the key to the selective catalytic reduction of Selective catalytic reduction of $NH_3$ ($NH_3$-SCR) method, which is commonly used in coal-fired power plants for abating nitrogen oxides ($NO_x$) in flue gas (Cheng et al., 2014). $V_2O_5$–$WO_3/TiO_2$ is the main commercial catalyst used in $NH_3$-SCR systems due to its high catalytic activity, high thermal stability and resistance to $SO_2$ (Forzatti, 2001). However, owing to the toxicity of $V_2O_5$ (Larsson et al., 2013), landfilling

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http://dx.doi.org/10.1016/j.jes.2015.12.039
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of spent SCR catalysts will not only waste metal resources but also pose potentially huge threats to the environment and human beings.

Due to the strict emission standards for $NO_x$, hundreds of coal-fired power plants have had to introduce de-$NO_x$ technology since 2012 in China. By 2014, all coal-fired power plants in China with a capacity of about 660 GW had installed de-$NO_x$ processes to reduce $NO_x$ emission. Among these, the $NH_3$-SCR process is dominant, and the total volume of catalysts in use was about 528,000 $m^3$. It can predicted that other industries (*i.e.* waste incinerators, cement kilns, steel industries) will also use $NH_3$-SCR technology in the future. Many impurities in flue gas can cause the deactivation of SCR catalysts, for example, alkali metals and alkaline earth metals (Kröcher and Elsener, 2008; Kamata et al., 1999; Chen et al., 2011), heavy metals (Kröcher and Elsener, 2008; Khodayari and Odenbrand, 1998), P (Castellino et al., 2008, 2009) and S (Crocker et al., 2004; Yu et al., 2016). Generally, an SCR catalyst has a lifetime around 2–7 years, depending upon its application and placement in power plants (Argyle and Bartholomew, 2015). Huge amounts of spent SCR catalysts will thus be produced, and their treatment will be a serious problem in the near future.

The regeneration of used catalysts will be a preferable option because it could prolong the lifetime of catalysts and thus save metal resources. Regeneration of three-way automobile catalysts (TWCs) and other catalysts has drawn much attention in recent years. (López et al., 2011; Christou et al., 2006, 2007; Subramanian et al., 2011; Christou and Efstathiou, 2013). However, research on regeneration of SCR catalysts has been limited. In our recent studies, we found that a combined method (*viz.* catalysts treated by dilute NaOH and $HNO_3$ solutions in sequence) was effective in regeneration of a deactivated SCR catalyst used in a coal-fired power plant (Yu et al., 2016). In addition, dilute $H_2SO_4$ solution was an effective method for regenerating SCR catalysts deactivated by alkali metals, and dilute $H_2O_2$ solution seemed to be effective in regeneration of catalysts poisoned by As (Shang et al., 2012; Peng et al., 2015; Li et al., 2015; Gao et al., 2014). Municipal waste incinerators have been used in many countries to get rid of waste. Unlike the flue gas from coal fired power plants, Pb is a typical element in the flue gas from municipal waste incinerators and could lead to the deactivation of SCR catalysts (Khodayari and Odenbrand, 1998; Jiang et al., 2014, 2015). However, research on regeneration of SCR catalysts deactivated by Pb has been rare. Thus, there is still a need to explore new methods for regeneration of SCR catalysts.

In this article, the regeneration of commercial SCR catalysts treated by mixed solutions containing $K_2SO_4$, $Na_2SO_4$, $CaSO_4$, $Pb(NO_3)_2$ and $NH_4H_2PO_4$ was investigated. $H_2SO_4$, oxalic acid, $HNO_3$, acetic acid and Ethylenediaminetetraacetic acid (EDTA) solutions were used to regenerate the deactivated samples. A novel method combining Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and $H_2SO_4$ solutions was also used for regeneration of deactivated samples. The activities of samples regenerated by different methods were compared and the fresh, deactivated and regenerated samples were characterized by $N_2$ adsorption–desorption, X-ray diffraction (XRD), X-ray fluorescence (XRF), $H_2$-temperature programmed reduction ($H_2$-TPR), scanning electron microscopy (SEM), $NH_3$-temperature programmed desorption ($NH_3$-TPD), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) and an inductively coupled plasma optical emission spectrometer (ICP-OES).

## 1. Experimental

### 1.1. Catalyst samples

The catalyst used in the experiment was a honeycomb commercial SCR catalyst with wall thickness of 0.90 mm and pitch of 7.70 mm. For sample preparation, fresh catalyst (Fresh) samples cut into pieces with 16 channels (about 3.2 × 3.2 × 5.0 cm) were impregnated with a 500 m L aqueous mixed solution containing $K_2SO_4$ (2 wt.%), $Na_2SO_4$ (2 wt.%), $Pb(NO_3)_2$ (2 wt.%), $NH_4H_2PO_4$ (2 wt.%) and $CaSO_4$ (saturated). The wet samples (De) were then dried in air at 120°C for 2 hr. followed by calcination at 600°C in air for 5 hr. The deactivated samples were first impregnated with 1 L regeneration solution for 5 min under ultrasound and then washed (continuous air stirring, 100 mL/min, 0.05 MPa) at 25°C for a certain time. Afterward, the samples were dried at 120°C for 2 hr. The detailed methods are shown in Table 1.

### 1.2. Activity measurements

The catalytic activity tests for SCR of nitric oxide (NO) by $NH_3$ were evaluated in a fixed-bed quartz reactor (Φ10 mm × 600 mm). The catalyst sample (20–40 mesh, 1.2 mL) was placed in the middle of the reactor. The total gas flow rate was 1250 mL/min (STP) and consisted of NO (700 ppm), $NH_3$ (700 ppm) and $O_2$ (4%) in $N_2$. A flue gas analyzer (T-350, Testo Company, Germany) was used to measure the concentrations of $O_2$ and NO. $N_2O$ at the outlet of the reactor was detected by gas chromatography (7890A, Agilent Technologies, USA). The conversion of NO was obtained by the following equation:

$$x = \frac{C_{NO,in} - C_{NO,out}}{C_{NO,in}} \times 100\% \quad (1)$$

where $C_{NO,in}$ and $C_{NO,out}$ are the NO concentrations of the simulated gas stream at the inlet and outlet of the reactor, respectively.

**Table 1 – Methods for regeneration of deactivated samples.**

| Sample | Method |
|---|---|
| Re-1 | 0.01 mol/L $H_2SO_4$, 30 min |
| Re-2 | 0.01 mol/L oxalic acid, 30 min |
| Re-3 | 0.01 mol/L acetic acid, 30 min |
| Re-4 | Saturated Ethylenediaminetetraacetic acid (EDTA), 30 min |
| Re-5 | 0.01 mol/L $HNO_3$, 30 min |
| Re-6 | 0.01 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.01 mol/L $H_2SO_4$, 15 min |
| Re-7 | 0.02 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.02 mol/L $H_2SO_4$, 15 min |
| Re-8 | 0.04 mol/L Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 15 min + 0.04 mol/L $H_2SO_4$, 15 min |