Deactivation of commercial Selective Catalytic Reduction (SCR) catalysts

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Introduction

Titania supported vanadia – tungstate substances represent the dominant catalyst deployed in selective catalytic reduction (SCR) systems for boilers [1, 2, 3]. These SCR catalysts promote NO_x reduction by ammonia and commonly operate at temperatures ranging from 300 – 400 °C. Deactivation of SCR catalysts has becoming an urgent issue to catalyst appliances as well as catalyst manufactures [3]. This investigation specifically focuses on the deactivation behaviors and mechanisms of commercial SCR catalysts, which have been exposed to flue gases from coal and biomass – fired systems.

Investigation of catalyst deactivation was conducted by comparing catalyst physical as well as kinetic characteristics. Changes of BET surface area, average pore diameter, topographic features, elemental compositions, and kinetic rate constants of NO_x reduction were compared with fresh and exposed SCR catalysts. The results indicate that the catalyst deactivation is a consequence of multiple deactivation mechanisms including pore plugging, masking, poisoning. The subsequent poisoning investigation on lab-prepared SCR catalysts indicate that poisons (alkali and alkaline earth metals) occupied primarily the catalyst Bronsted acid sites, which functions together with vanadia sites, a redox sites, as a dual – site active center [4]. The match between decreases of kinetic constants and the loss of IR peak areas of Bronsted acid sites due to poisoning further confirms the suggested poisoning mechanism.

Materials and Methods

Commercial SCR catalysts from different venders were cut into small pieces for characterizing catalyst surfaces and measuring intrinsic kinetic constants. Catalyst BET surface area and pore size distribution were measured using nitrogen adsorption at liquid nitrogen temperature. Catalyst surface topographic features and elemental composition analyses were monitored with scanning electron microscope (SEM). NO_x reduction rate constants of fresh and exposed catalysts were determined using a model at various temperatures. The reactant gas contains 1000 ppm NH_3, 1000 ppm NO, 2% O_2, 10% H_2O, helium balance, GHSV = 15,000 h^{-1}.

1% V_2O_5 - WO_3 / TiO_2 catalysts were prepared by an incipient wetness impregnation method followed by drying and calcination. Potassium, sodium, and calcium, with a metal to vanadia ratio of 0.5:1, were subsequently deposited onto 1% V_2O_5 - WO_3 / TiO_2 by impregnation. After drying and calcinations, fine contaminated catalyst sample pressed into wafers provide an active surface for in situ FTIR-MS reactor investigation. Ammonia adsorption indicates changes of Bronsted acid population before and after contamination, and

intrinsic kinetic investigation compares NO_x reduction rate constants at various temperatures on fresh and contaminated catalysts.

Results and Discussion

The BET surface areas of commercial SCR catalysts M1 and M2 decreased after 2063 and 3800 hour of exposures to flue gas from low – rank coal – fired boilers, as well as 350 hour to effluent from coal-biomass co-fired boilers. The average pore diameter, however, increased slightly with various exposures as illustrated in Table 1.

Table 1. Surface composition via ESCA

Samples	M1		M2	
	BET surface area, m^2/g	Average pore diameter, nm	BET surface area, m^2/g	Average pore diameter, nm
Fresh	61.5 ± 0.2	16.4	56.6 ± 0.1	13.3
2063	53.5 ± 0.2	17.5	54.5 ± 0.1	13.6
3800	55.6 ± 0.1	17.7	50.0 ± 0.1	17.7
Biomass	48.2 ± 0.1	19.9	43.9 ± 0.1	20.0

The decrease of BET surface areas and increase of pore diameter indicate that pore plugging and masking occurred on exposed catalyst surfaces, which is verified by SEM and surface elemental analyses that ash deposited on catalyst surface, as shown in Figure 1, and $CaSO_4$, sodium and magnesium salt formed on catalyst surface as indicated in Figure 2. The elemental composition data in Figure 2 were collected on relatively clean catalyst surface where no ash particles included, therefore the data was not a reflection of ash particles composition, but an indication of new layers of $CaSO_4$, sodium, and magnesium salt formed on catalyst surface.
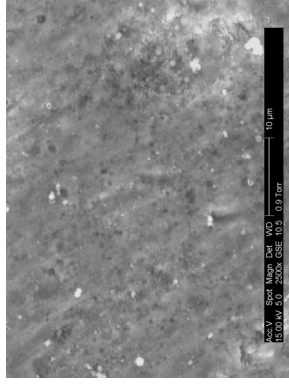

Figure 1 SEM image of ash deposited on exposed catalyst

Except deposition, alkali and alkaline earth metals also possess the potential of migration into the inner catalyst surface where most of the active sites locate, especially when temperature drops below water dew point which occurs during boiler start up and shut down, under which circumstances, metal migration is expedited, and poisoning occurs.

is represented by the IR peak area of the 1421 cm^{-1} IR band. The match between catalyst activity loss and IR peak area loss along with the standard parity line strongly suggests that the mechanism of poisoning is that poisons occupy Brønsted acid sites, which is one site of a dual-site active center, an acid-redox active center, for vanadia SCR catalyst [2, 4].

Figure 4 Parity line plot of activity loss and IR peak area loss.

However, Brønsted acid site does not possess NO$_x$ reduction activity as indicated by zero reaction rates on WO$_3$/TiO$_2$, shown in Figure 5.

Figure 5 Kinetic rate constants comparison of 1% V – 9% W/TiO$_2$, 1%V/TiO$_2$, and 9% W/TiO$_2$.

References
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Figure 2 Fresh and exposed M1 catalyst surface element composition comparison

NO$_x$ reduction was examined on fresh and various exposed commercial catalysts. Figure 3 demonstrates the rate constants calculated and adjusted with respect to the available catalyst surface area as illustrated in Table 1. Comparisons of NO$_x$ reduction rate constants of fresh and exposed commercial SCR catalysts at a temperature range of 250 – 330 °C indicate that: (1) SCR catalysts lost activities progressively with exposure (2063 hour *vs.* 3800 hour); (2) Catalyst deactivation mechanism differs with various effluents of boilers (coal *vs.* biomass), (3) plugging and poisoning both contribute to catalyst deactivation. For instance, the surface areas and average pore diameters of M1 2063 and M1 3800 remained similar enough (Table 1) that the additional activity loss of M1 3800 should arise from other reasons such as poisoning.
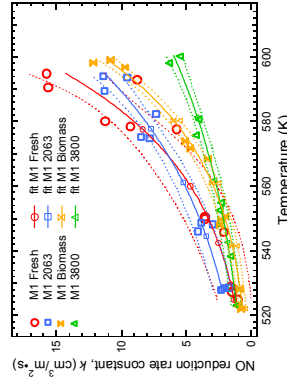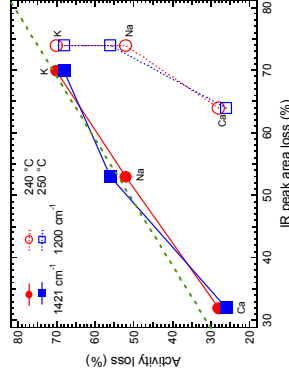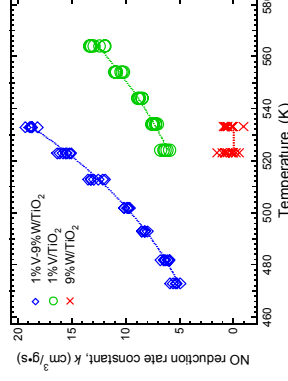
Figure 3 Comparison of M1 kinetic constants as a function of temperature and exposure in a slipstream reactor with 95% confidence intervals

Significance

The subsequent investigation of poisoning was conducted on lab-prepared SCR catalysts. The intrinsic kinetic rate constants of NO$_x$ reduction were determined with a Mass Spectrometer. Ammonia adsorption at ambient temperature monitored by *in situ* FT – IR revealed information about the amount and strength of catalyst surface acid site. Figure 4 compares the loss of catalyst activity and the decrease of Brønsted acid sites population, which