

## Experimental Deactivation Analysis of Commercial Selective Catalytic Reduction (SCR) Catalysts

Xiaoyu Guo<sup>1</sup>, John Ashton, Jacob Butler, Aaron Nackos, William C. Hecker, Calvin H. Bartholomew, and Larry L. Baxter<sup>2\*</sup>,

<sup>1</sup>(*Italics, 8pt*) Babcock & Wilcox Research Center, Barberton, Ohio 44203 (USA)

<sup>2</sup> Brigham Young University, Provo, Utah, 84602 (USA)

\*[larry\\_baxter@byu.edu](mailto:larry_baxter@byu.edu) (corresponding author designated with a star)

### Introduction

Titania-supported, vanadia-tungstate catalysts dominate selective catalytic reduction (SCR) systems for boilers [1, 2, 3]. These SCR catalysts promote NO<sub>x</sub> reduction by ammonia and commonly operate at temperatures ranging from 300 – 400 °C. Deactivation of SCR catalysts has become an urgent issue to catalyst users and manufactures [3]. This investigation specifically focuses on the deactivation rates and mechanisms of commercial SCR catalysts which have been exposed to flue gases from coal-, biomass- and co-fired systems. Commercial and laboratory data provide the basis for this analysis.

Experimentally determined physical and kinetic characteristics provide the dataset from which mechanisms and rates are determined. Changes of BET surface area, average pore diameter, topographic features, elemental compositions, and kinetic rate constants of NO<sub>x</sub> 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, and poisoning. The subsequent poisoning investigation on laboratory-prepared SCR catalysts indicates that poisons (alkali and alkaline earth metals) primarily occupied the catalyst Brønsted acid sites, which function together with vanadia sites and redox sites as a dual-site active center [4]. The correlation between decreases of the value of kinetic constants and the corresponding IR peak areas of Brønsted acid sites due to poisoning further confirms the above indication.

### Materials and Methods

Sampled sections of 5 different commercial SCR catalysts exposed for up to 3800 hours to slip streams from commercial boilers in a temperature- and velocity-controlled reactor provided the means to monitor changes in 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 a scanning electron microscope (SEM). NO<sub>x</sub> reduction rate constants of fresh and exposed catalysts were determined using a model at various temperatures with a reactant gas comprising 1000 ppm NH<sub>3</sub>, 1000 ppm NO, 2% O<sub>2</sub>, 10% H<sub>2</sub>O, helium balance, GHSV = 15,000 h<sup>-1</sup>.

1% V<sub>2</sub>O<sub>5</sub>-9%WO<sub>3</sub>/TiO<sub>2</sub> catalysts were prepared by an incipient wetness impregnation method followed by drying and calcination. Potassium, sodium, and calcium, with a metal to vanadium ratio up to 0.5:1, were subsequently deposited onto 1% V<sub>2</sub>O<sub>5</sub>-9%WO<sub>3</sub>/TiO<sub>2</sub> by impregnation. After drying and calcination, fine contaminated catalyst sample pressed into wafers provide an active surface for *in situ* FTIR-MS reactor investigation.

Ammonia adsorption indicates changes of Brønsted acid population before and after contamination, and intrinsic kinetics investigations compare NO<sub>x</sub> reduction rates and kinetic constants at various temperatures on fresh and contaminated samples.

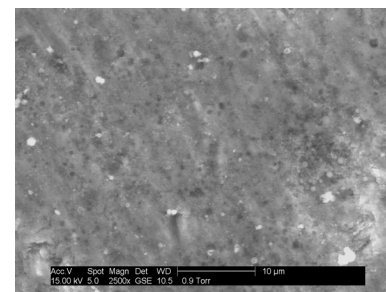
### Results and Discussion

The BET surface areas of commercial SCR catalysts M1 and M2 decreased after 2063 and 3800 hours of exposure to flue gas from low-rank coal-fired boilers, as well as after 350 exposure hours 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**

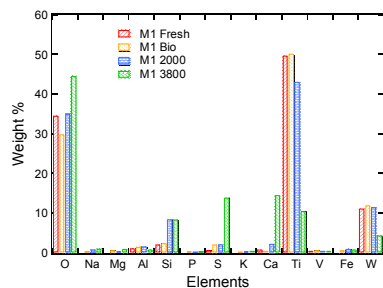
Samples	M1		M2	
	BET surface area, m <sup>2</sup> /g	Average pore diameter, nm	BET surface area, m <sup>2</sup> /g	Average pore diameter, nm
Fresh	61.5 ± 0.2	16.4	56.6 ± 0.1	13.3
2063	53.5 ± 0.2	17.5	54.5 ± 0.1	13.6
3800	55.6 ± 0.1	17.7	50.0 ± 0.1	17.7
Biomass	48.2 ± 0.1	19.9	43.9 ± 0.1	20.0

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, as shown in Figure 1. Calcium, sodium and magnesium salts (primarily sulfates) 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 accumulated, therefore the data are not a reflection of ash particle composition, but an indication of new layers of mostly CaSO<sub>4</sub> and smaller amounts of sodium and magnesium salt formed on the catalyst surface.



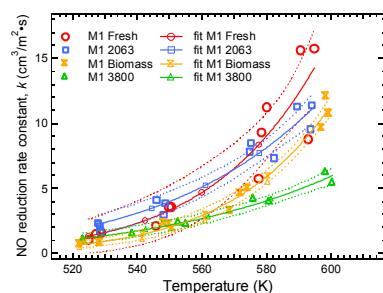
**Figure 1** SEM image of ash deposited on exposed catalyst

Except deposition, alkali and alkaline earth metals also possess the potential to migrate into the inner catalyst surface where most of the active sites locate, especially when the temperature drops below the water dew point, which occurs during boiler start up and shut down. This could lead to increased poisoning.



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

NO<sub>x</sub> reduction was examined on fresh and various exposed commercial catalysts. Figure 3 demonstrates the rate constants calculated and adjusted for available catalyst surface area as indicated in Table 1. Comparisons of NO<sub>x</sub> reduction rate constants of fresh and exposed commercial SCR catalysts in the temperature range of 250 – 330 °C indicate that: (1) SCR catalysts lost activities progressively with exposure time (2063 hour vs. 3800 hour), (2) different boiler fuels induce different deactivation patterns (coal vs. biomass), (3) plugging and poisoning both contribute to catalyst deactivation (surface area change indicates plugging while kinetic change adjusted for changed surface area indicates poisoning). In the case of M1 2063 and M1 3800, the surface area and average pore diameter remained essentially constant (Table 1) indicating that the additional activity loss arises from poisoning and that poisoning continues to increase after plugging is largely stabilized.

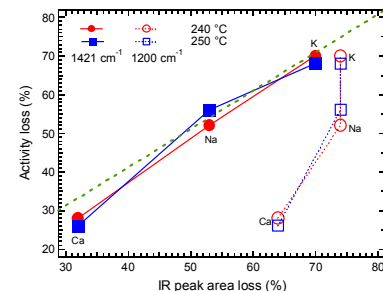


**Figure 3** Comparison of M1 kinetic constants as a function of temperature and exposure in a slipstream reactor with 95% confidence intervals

#### Significance

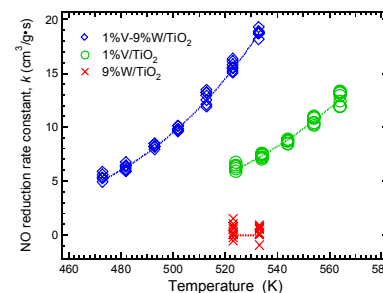
The subsequent investigation of poisoning was conducted on lab-prepared SCR catalysts. The intrinsic kinetic rate constants for NO<sub>x</sub> reduction were determined using mass

spec data for gas concentrations. Ammonia adsorption at ambient temperature monitored by *in situ* FT – IR spectroscopy reveals the amount and strength of catalyst surface acid sites. Figure 4 compares the activity loss and Brønsted acid sites population as indicated by the IR peak area at 1421 cm<sup>-1</sup>. The correlation 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 for a vanadia SCR catalyst – acid-redox active center [2, 4].



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

However, Brønsted acid sites do not possess activity in isolation, as indicated by the zero reaction rates on WO<sub>3</sub>/TiO<sub>2</sub>, shown in Figure 5.



**Figure 5** Kinetic rate constants comparison of 1% V – 9% W/TiO<sub>2</sub>, 1%V/TiO<sub>2</sub>, and 9% W/TiO<sub>2</sub>.

#### References

1. Topsøe, N.Y. *Journal of Catalysis* 151, 226 (1995).
2. Lietti, L., Nova, I. *Journal of Catalysis* 187, 419 (1999)
3. Due-Hansen, J., Kustov, A.L. *Appl. Catal. B: Environmental* 66, 161 (2006)
4. Wachs, I.E., Weckhuysen, B.M. *Appl. Catal. A: General* 157, 67 (1997)