

Influence of Biomass Co-Firing on SCR Catalyst Deactivation

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Abstract

SCR catalyst from a coal-fired power plant (Poland) was characterized in order to identify the deactivation processes. The received monoliths of DeNO_x catalyst, with yellow-light green shades, were TiO₂ supported V₂O₅ catalyst modified with tungsten oxide (V₂O₅-WO_x/TiO₂). Four samples with different operation times (fresh, 3, 6 and 12 months) showing a maximum deactivation of 25% (approximately) were characterized in order to identify the deactivation processes. The catalysts monoliths showed partial plugging of channels with fly ashes (cenospheres). This occurrence can be partially responsible for the activity decay since part of the catalyst bed become unavailable. The elemental analysis performed for fresh and post reaction catalyst, by AAS and EDS during SEM, showed deposition of alkali elements (Na, K, Ca) which promotes a decrease of the surface acidity evaluated by 1-butene to 2-butene isomerization. The UV-Vis spectra showed only minor changes on the vanadium oxidation state whereas XRD remains unchangeable for all the analyzed catalysts and were mainly ascribable to the support material (TiO₂). The physical-chemical characterization of the fresh and post reaction catalysts seem to point out the alkali deposition as the main deactivation process for the SCR studied catalyst.

Keywords: *NO_x, static sources, SCR catalysts, V₂O₅-WO_x/TiO₂, deactivation, fly ashes, alkali deposition*

1. Introduction

Electric energy is one of the most desirable goods in modern world. Many techniques have been developed for its production but a majority of power plants are still based on fossil fuels combustion. Among gas, oil and coal, the solid fuels have the biggest share in electric energy production. Lignite and hard coal combustion units are highly developed nowadays, the modern ones operating at >40% of overall efficiency. Even with sophisticated technology there are still drawbacks, mostly caused by the used fuel. The most important one is environmental impact of coal-based power plants. Heat produced in coal combustion is the most desirable effect of fuel oxidation. It is accompanied by transforming coal, including its moisture and mineral matter attached, into exhaust gases, bottom ash and fly ash. Each has to be treated in a proper way to minimize the impacts on the environment. Exhaust gases are responsible for air pollution problem. Most dangerous are SO₂ and NO_x. They are only a small fraction of entire exhaust gases volume, but taking into account huge amounts of flue gases released by every power plant a year, they are becoming a significant threat to be dealt with. This is the reason why European Union Commission is setting the emission limits to both of those gases, as well as other pollutants being by-products of combustion process. There are two important documents that point how modern power plant should operate. First one is European Commission Directive, which sets emission limits for every specified production unit, depending on size and type of fuel used. The most recent Directive connected to power plants is 2010/75/UE.

Second one is Best Available Techniques (BAT), which is proposing techniques needed to achieve limits described in the first one. One of the means for decreasing NO_x emissions is selective catalytic reduction (SCR), using ammonia and catalyst to convert nitrogen oxides to elemental nitrogen and water. It was proven to be the most efficient post combustion method, and it is used in many units around the world with success. Apart from NO_x and SO₂, carbon dioxide, one of by-products causing great concern, as it is one of the greenhouse gases, molecules that may lead to climatic changes. Despite the fact that there are many natural sources of CO₂, it has been stated that the rising levels of carbon dioxide in the atmosphere are to a great extent influenced by the combustion of fossil fuels, including coal. Coal and lignite have the biggest share in CO₂ formation per unit of electricity produced from their combustion. One way of reducing carbon dioxide emissions is to use biomass as a part of the fuel mixture. It has been proven that it is possible to co-fire coal with biomass in powerplants without major retrofits, even if biomass has worse combustion properties than traditional fuels. This work aims to study the influence of biomass co-combustion on the performance and deactivation of commercial DeNO_x catalyst used in a full scale boiler of the existing power plant. [1, 2, 3]

2. Techniques of NO_x emission reduction

There are two groups of techniques used to reduce NO_x emissions. Primary methods are concentrated on reducing NO_x formation rate during combustion. It is achieved by changing conditions inside the boiler, such as flame temperature, amount of oxygen and combustion volume. Primary methods are considered to be cheaper than secondary ones, but they offer lower reduction efficiency. Secondary methods use chemical reaction to reduce already created NO_x. They use a reducing agent in quantities depending on the boiler power, and thus the running costs of a power plant can significantly increase. This group of methods is considered more expensive but it grants higher efficiency. [1]

Primary methods:

- low excess air – lowering amount of air used in combustion (10-40%)
- air staging – dividing stream of air into two zones (10-70%)
- flue gas recirculation – 20-30% of flue gas is recirculated into combustion zone (20% coal, 50% gas)
- reduced air preheating – lower temperature of air used for combustion (20-30%)
- fuel staging – dividing fuel stream into three zones (50-60%)
- low NO_x burners – changing air and fuel mixing process in burners (25-60%)

Secondary methods:

- selective catalytic reduction – reduction of NO_x with NH₃ on catalyst (80-95%)
- selective non-catalytic reduction – reduction of NO_x with NH₃ without use of catalyst (ca. 50%)

The newest directive concerning (among others) NO_x emission level is EU Directive 2010/75/EU. The allowed emissions depend on the type of fuel used and the nominal power of the installation in question, as illustrated by Table 1.

Table 1 Emission limits for power plants in mg/Nm³ of NO_x [2]

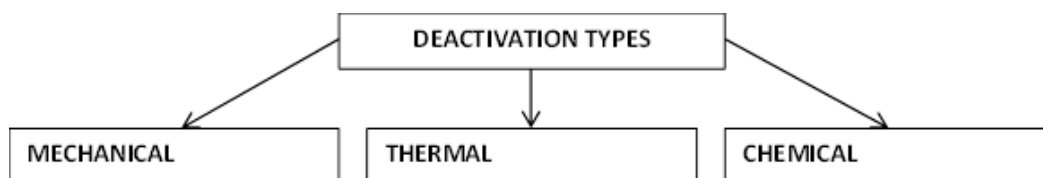
Nominal power in fuel[MW]	Coal, lignite and other solid fuels	Biomass and peat	Liquid fuels
50-100	300	300	450
	450 for lignite		
100-300	200	250	200
>300	200	200	150

3. Catalysts

Selective catalytic reduction (SCR) of NO_x with ammonia is the most efficient method of NO_x emissions reduction and it is widely used in EU, USA and Japan. The most often applied catalyst consists of vanadium on titanium support, with the addition of WO₃ to increase the temperature window, SiO₂ to stabilize the structure and MoO₃ to make the catalyst more resistant towards poisoning by SO₂. There are four catalyst types used in SCR:

- base metal oxides, which consist of the support material (TiO₂), together with the active components vanadium, tungsten, molybdenum. This type of catalyst has best efficiency in temperature range of 300 – 450 °C.
- zeolites, which are crystalline, highly porous natural or synthetic alumino-silicate three-dimensional structures. Catalysts based on zeolites are used at temperatures between 350 and 600 °C.
- iron oxides, which consist of iron oxide particles with a thin crystalline cover of iron phosphate
- activated carbon, as for example in Mitsui method [<http://www.mitsui-mining.co.jp/index2.html>]. Due to thermal instability of activated carbon at higher temperatures, low operating temperatures of 100 – 220 °C are required. As a result, in power stations, activated carbon can be employed in the 'tail-end' configuration, because only this setting guarantees proper thermal conditions.

The catalysts are usually integrated into the flue gas cleaning chain in the so-called „high-dust” position, upstream of electrostatic precipitator. This leads to catalyst deactivation which is a major drawback. There are several mechanisms of deactivation, resulting from the presence of pollutants other than NO_x in the cleaned flue gases. Of those, especially ash and SO₂, which may lead to fouling and poisoning, are important. The problem of deactivation by SO₂ has been well recognized and led to the improvement of the catalysts, by the addition to the industrial catalysts of small amounts of WO₃ or MoO₃ which decreases the rate of SO₂ oxidation into SO₃ and thus the extent of poisoning.



- ash deposition
- monolith channel blocking
- phase change of support
- phase change of active substance
- poisoning of active substance by flue gas and ash

4. Experimental

The catalyst was a commercial honeycomb (proprietary one, undisclosed). It was exposed to flue gas in the industrial pulverized coal boiler. Over the studied period the boiler co-fired coal and biomass. The types of biomass used were wood pellets and sunflower pellets with typical composition shown in Table 2. The exposure time was 2270, 4527 or 9405 h.

Table 2 Typical composition of biomass used for co-combustion

	C	H	O	N	S
Wood	51.03	6.06	42.31	0.08	0.02
Sunflowe	49.87	5.82	38.16	1.06	0.19



Figure 1 Catalyst monolith

The catalysts were prepared for characterization in the powder form. A part of each monolith (fresh, and after specific exposure) was ground in an agate mortar manually, after collecting non-bonded fly ash from the samples 3M, 6M and 12M. Each ground sample consisted of inner and outer parts of the monolith in the appropriate proportions. Ash samples scraped from the catalysts were additionally tested, in order to compare the content of certain relevant elements.

The content of selected elements in catalyst and ash samples was determined by AAS using Hitachi Spectrophotometer Z-2000 with Zeeman effect background correction and hollow cathode lamp as the source of radiation. Morphology of fresh and exposed catalysts were examined by SEM (Joel JSM7001F FEG-SEM over double face carbon adhesive (analytical grade), covered with a thin film of graphite. Phase composition of both catalysts and ash samples was studied using PANalytical Empyrean diffractometer using CuK α radiation ($\lambda = 154.05$ pm) at room temperature. To identify changes of active phase in exposed catalyst samples UV-Vis was performed on Cary 5000 Varian equipment with a DRA 2500 diffuse reflectance accessory. Infrared spectra of

the all catalysts and ashes were collected with a resolution of 16 cm^{-1} , using a FT-MIR equipment from BOMEN (FTLA2000-100, ABB) with a DTGS detector. A horizontal total attenuated reflection accessory (HATR), from PIKE Technologies, with a ZnSe crystal was applied. Sixty-four scans were accumulated for each spectrum to obtain an acceptable signal-to-noise ratio. Acidity of catalyst samples was determined by butene isomerisation method.

The activity of the fresh and poisoned catalysts was determined additionally by EDF Polska outside the power station (as it does not contain an SCR installation). The relative loss of activity discussed in this work is defined as:

$$\Delta x = \frac{(x_0 - x_t)}{x_0} * 100\%$$

Where: Δx – relative loss of activity

x- conversion

indices: 0 – fresh catalysts, t– catalyst after time t of exposure: 2270, 4527 or 9405 h

5. Results and discussion

5.1 Conversion

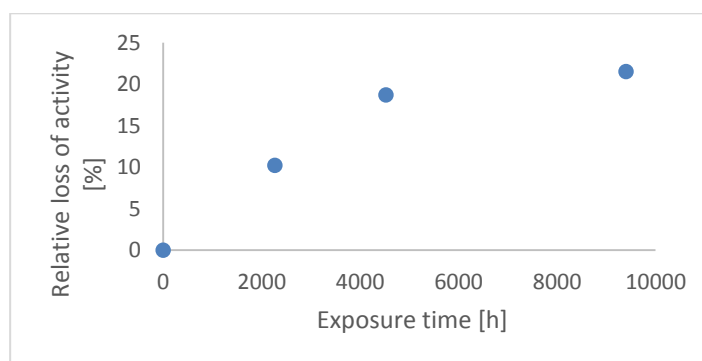


Figure 2 Relative loss of activity of the studied catalysts

Major loss of activity was observed for the first period of exposure of ca. 6 months (ca. 18.7 % out of total 21.5 % during 12 months). The activity decrease during the next 6 months was equal. It is possible to draw a straight line through the first three experimental points, with $R^2=0.9969$, including the fresh catalyst with relative decrease of activity equal to zero, while there is no correlation for all four experimental points ($R^2 =0.7378$). Taking into account the tendency registered for the first 6 months, the average relative loss of activity for the catalysts studied in this work was ca 4.2 %/1000 h. Even taking into account that during the last two months of the operation of the installation only coal was fired (without the addition of biomass), the 12 M catalyst showed the decreasing effect of poisoning in comparison to 3M and 6 M.

5.2 AAS

Table 3 Catalyst composition results from AAS

	0M %	3M %	6M %	12M %
Ca	0.84	1.03	1.12	0.80
Fe	0.04	0.04	0.05	0.53
Mg	0.09	0.09	0.11	0.44
K	0.02	0.10	0.18	0.63
Na	0.01	0.06	0.11	0.34

Table 4 Ash composition results from AAS

	3M ash [%]	6M ash [%]	12M ash [%]
Si	41.73	41.11	49.32
Al	20.35	16.99	20.44
Ca	7.47	4.37	3.16
Fe	6.37	6.87	6.09
Mg	2.72	2.63	2.20
K	2.42	2.43	2.71
Na	0.52	0.65	0.67

Fresh catalyst had only traces of iron, magnesium, potassium and sodium, and a relatively high content of calcium. The exposed catalyst samples were enriched in K and Na, two elements considered the as the greatest poisons of vanadium-based catalysts. The amount of calcium changed only slightly during the whole exposure time. Taking into account the composition of the fresh catalyst, it may be assumed, that this element was inherent to the catalyst and only to a small extent may have arised from the ash samples, although wood pellets contain Ca. The study of Koukouza et. al showed that the fly ash from the traditional fuel contained up to 1.67% of potassium while the pure biomass might contain over 12% of K. It must be pointed out however, that the discussed power plant used a variety of biomass and different types of biomass have different composition. [4]

5.3 SEM & EDS

Table 5 The comparison of the content of K, Na and S from EDS measurements

	0M	3M		6M		12M		Ash	
	I	I	II	I	II	I	II	I	II
	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%
S	0.36	0.83	0.43	0.29	0.44	1.16	0.98	0.98	1.55
K	0	0	0	0	0	0.35	0	1.49	1.2
Na	0	0	0	0	0	0	0	0.34	0

In order to analyse the elemental composition and compare the results with those from AAS, EDS analysis was carried out. Additionally, EDS was used to obtain information about the content of another very important poisoning element that may be present on the surface that is sulphur. For each sample the EDS analysis was carried out at two selected places. To compare the elemental composition, concentrations of most important elements for each sample and selected place were summarized in Table 5. For every sample a typical place with the composition including Ti, V, W, O and thus identifying it as a part of catalyst was found. Additionally most analysed places contain carbon. However, it is not possible to determine if it is unburned fuel because of the procedure of sample preparation for SEM. Apart from the pollutants already identified by AAS i.e. K and N, considerable amounts of S were identified by EDS. Sulphur is present even in the fresh catalyst.

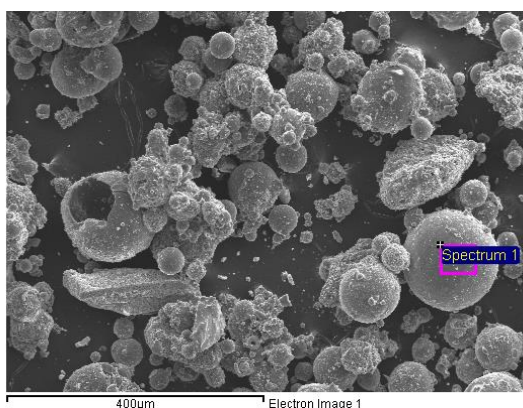


Figure 3 SEM image of 6M ash sample

SEM image of ash presents spherical particles, including empty broken sphere. These may be cenospheres which are often observed as a component of fly ash from coal combustion. Their composition includes typical mineral matter elements, such as silicon, aluminium, magnesium and calcium. Additionally to cenospheres, other ash particles with less regular shapes may be observed.

5.4 XRD

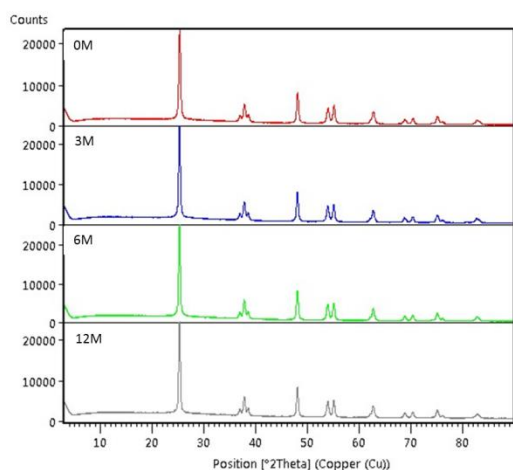


Figure 4 XRD of the studied catalysts

Figure 4 shows the same reflections for all catalyst samples, which were identified as TiO_2 (anatase). No reflections corresponding to vanadium or tungsten crystalline phases were observed. Vanadium oxide crystalline phase reflections are expected at $2\theta=20.15^\circ$, 26.10° and 31.06° and for tungsten oxide at $2\theta=24^\circ$ and 28° . No change in the support itself proves that even after twelve months of exposure the transformation of anatase to rutile did not take place.

Table 6 Compounds present in ash samples

Compound name	3M ash	6M ash	12M ash
CaSO ₄ anhydrite	+	+	+
SiO ₂ quartz	+	+	+
Mullite	+	+	+
Corundum	-	+ -	-
Andradite	-	+ -	-
Sillimanite	+	+	+
Anorthite	-	-	-
Cristobalite	-	-	-
Gehlenite	-	+ -	-
Periclase	-	+	-
Magnesium ferrite	+ -	+	+ -
TiO ₂	-	-	-
K ₂ SO ₄	-	-	-
KCl	-	-	-

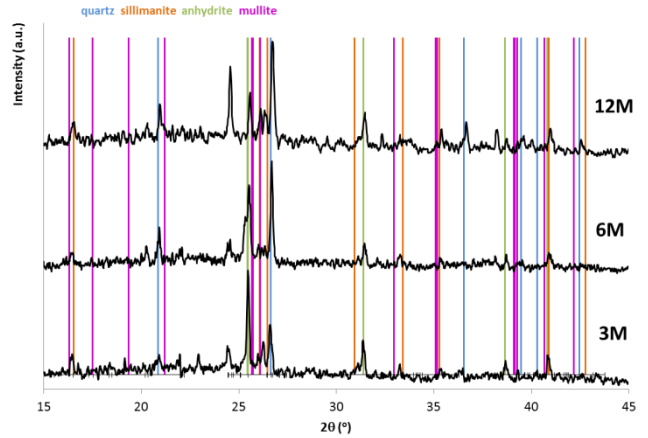


Figure 5 XRD pattern for 3M ash sample

The XRD patterns for ash collected from catalysts samples, after different times of exposure, show the presence of a certain amount of amorphous phase, as well as the following crystalline compounds: anhydrite (CaSO₄), quartz (SiO₂), mullite (3Al₂O₃2SiO₂ or 2Al₂O₃ SiO₂), sillimanite (Al₂SiO₅) and in case of 6M-ash also magnesio-ferrite (Mg(Fe)₂O₄). Sahu et al. (Renewable and Sustainable Energy reviews, 39 (2014) 575), claimed that different fuel characteristics, the gas atmosphere and the used combustion technology, influenced the composition of fly ash. [5]

5.5 UV-vis

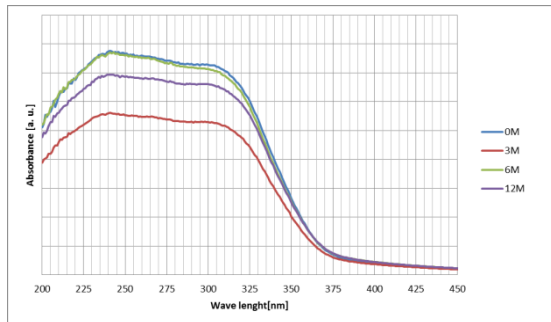


Figure 6 UV-Vis spectra of fresh, 3M, 6M and 12M sample

For each sample there are two absorption bands. The first, with a maximum at

ca. 240 nm, is most probably the charge–transfer transition of catalyst support $Ti^{4+} \rightarrow O^{2-}$ [6]. The second maximum is located at ca. 320 nm and it represents charge transfer of O^{2-} to V^{5+} in tetrahedral species [7]. The absence of any band shifts in comparison to the fresh catalyst allows to assume, that neither titanium support nor active vanadium phase were changed during the exposure under industrial conditions of biomass co-fired coal power plant [8].

5.6 FTIR

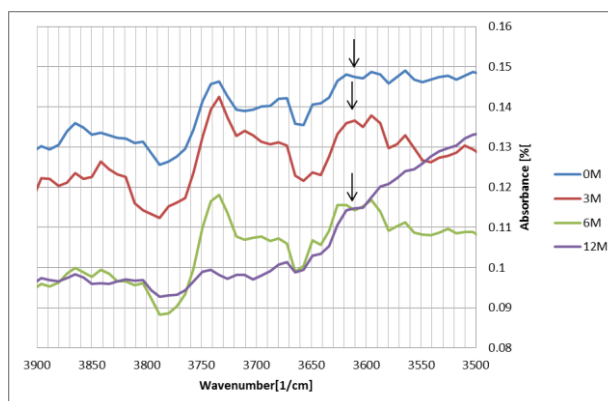


Figure 7 FTIR spectra of tested catalyst samples

Bands at 3615cm^{-1} were identified in literature [Baran et al. 2013] as vibration of V-OH group [8].

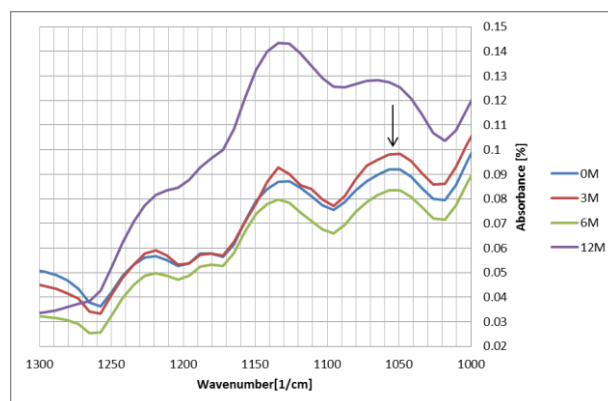


Figure 8 FTIR spectra of tested catalyst samples

The band at 1035cm^{-1} has been identified as stretching vibration of V=O groups [9].

5.7 Butene isomerization

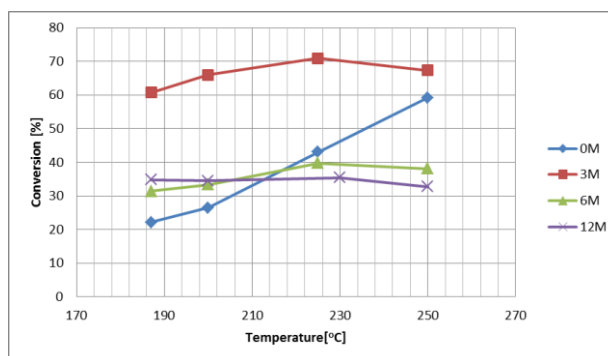


Figure 9 Conversion of 1-butene to 2-butene as a function of temperature

For the fresh catalyst the reaction rate increased with the rising temperature almost linearly from 20% to 60% at 250°C . Surprisingly high conversion was obtained for the catalyst after three months of exposure. These additional acid sites which raised the conversion of 1-butene to 2-butene for 3M catalyst most probably arise from the formation of surface sulphate (VI) species. [10]

Conclusions

The aim of this work was to investigate the influence of biomass addition to fuel on SCR catalyst. What differed this study from many other DeNO_x catalyst investigations, were the examined samples. Thanks to cooperation with EDF Polska, there was an opportunity to examine commercial honeycomb SCR catalyst deactivated under industrial conditions in the full scale coal-fired boiler. EDF Polska provided the data about the biomass type and share, as well as about conversion of NO for both fresh and exposed catalysts, allowing the conclusions concerning the extent of deactivation. In the presented MSc thesis, fresh and deactivated catalysts were characterized and compared to the data from literature obtained in the laboratory-scale studies. The fresh and exposed catalysts were tested outside the power station and the relative decrease in activity of ca. 4.2 %/1000 h was found during ca. 4500 h. Afterwards, the degree of deactivation slowed down.

The catalysts and the ash collected from the catalysts were characterized by AAS, SEM, XRD, UV-Vis and acidity measurements. From the obtained results it may be concluded that:

- Alkalis were the main poison arising from the co-combustion. The increased amounts of K^+ , Na^+ and Mg^{2+} were found on the exposed catalysts, as well as in the fly ash collected from the catalysts. The content of Ca was not significantly increased. The main reason for potassium poisoning are relatively low Tamman temperatures of KCl and K_2SO_4 in the aerosols present in flue gas, leading to the deposition of these compounds on the particles of fly ash.
- The morphology of the catalysts was not influenced.
- The support (anatase) structure was stable under the industrial conditions.
- Vanadium isolated species were registered in both fresh and exposed catalysts. In neither of them polymeric species were found. The exposure to real flue gas did not change the oxidation degree of vanadium
- The acidity of the catalysts was increased during the first ca. 2300 hours, due to the formation of sulfate groups. They may have played a positive role at the initial period of exposure to flue gas, decreasing the extent of deactivation by potassium. Sulfate groups are characterized by stronger acidity than V-OH sites of SCR catalysts and thus may preferentially bind potassium. For the longer periods of exposure, poisoning of V-OH and V=O sites by potassium, plays more and more dominant role, resulting in the deactivation of the catalysts.

The information obtained for the catalysts exposed to flue gas under industrial conditions, may influence the choice of biomass and possibly influence the future strategy for the commercial catalysts regeneration. Some additional data, however, will be needed, especially the surface composition. The regeneration processes could be similar to those suggested in literature, e.g. washing with aqueous solutions of certain acids, to remove K^+ cations from the surface.

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