

Deactivation of SCR catalysts by potassium poisoning

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Introduction

Selective catalytic reduction (SCR) of NO_x with NH₃ is a well established method for controlling NO_x emissions from stationary sources such as coal fired heat and power plants [1]. In a time with great focus on the release of green houses gases such as CO₂ to the atmosphere firing (or co-firing) of biomass (straw, wood chips, etc.) is being applied in order to reduce the net CO₂ emissions. Unfortunately, the industrially applied SCR catalysts, typically consisting of V₂O₅ promoted with WO₃ on a TiO₂ carrier, have a significantly reduced lifetime when used on plants firing such fuels. This is due to an accelerated deactivation by a high amount of alkali metals, mainly potassium, present in most biomass [2]. While the effect of alkali metal on commercial SCR catalysts is generally understood, a more systematic study of the deactivation mechanism will provide useful information during development of new alkali resistant catalysts and/or improved means of operation.

Materials and Methods

Several series of plate shaped catalysts have been exposed to potassium (K) rich aerosols in a bench scale reactor described in detail in [2]. The catalysts, obtained from Haldor Topsøe A/S, consisted of samples of varying composition with respect to V₂O₅ and WO₃ in order to provide information on the influence of catalyst composition on the rate of deactivation. Parameters such as exposure time, operating temperature and/or aerosol particle size distribution have been varied between each exposure experiment. The catalytic activities of the exposed samples, as well as un-exposed counterparts, were measured in a fixed bed reactor at temperatures between 250 and 400 °C using a total gas flow of 2800 NmL/min composed of 500 ppmv NO, 600 ppmv NH₃, 5 vol.% O₂, about 1.4 vol.% H₂O and balance N₂. In order to study the transport of potassium in SCR catalysts, pellets consisting of three layers of crushed plate catalyst in close contact have been produced. One end layer was made from a 3%V₂O₅-7%WO₃/TiO₂ catalyst impregnated with K to a level of 0.8 wt.% while the other end layer consisted of an un-doped version of the same catalyst. The layer in between was either made from MgO, which ultimately may be used as an alkali resistant coating [3], or un-doped catalyst. The pellets were heat treated at 350 °C in a flow of 6 vol.% O₂, 3 vol.% H₂O and balance N₂. The K profiles through the three layers were recorded by SEM-EDS.

Results and Discussion

The relative activities at 350 °C of the exposed catalysts are given in Table 1 together with the conditions (K aerosol source, temperature, time, as well as the mode of the resulting mass based aerosol size distribution), at which the samples were exposed.

Table 1. Exposure conditions and relative activities of V₂O₅-(WO₃)/TiO₂ catalysts.

V ₂ O ₅ content (wt. %)	K source	Temperature (°C)	Time (h)	Distribution mode (μm)	Relative activity at 350 °C (%)	
					0 wt.% WO ₃	7 wt.% WO ₃
1	KCl	350	600	0.12	24	11
3	KCl	350	600	0.12	19	2
6	KCl	350	600	0.12	1	4
1	KCl	150	300	0.12	77	29
3	KCl	150	300	0.12	32	52
6	KCl	150	300	0.12	47	34
3	K ₂ SO ₄	150	240	1.3	77	64

While the activity of a WO₃ promoted catalyst generally is higher than that of an un-promoted one with the same V₂O₅ content, the relative activity drop upon exposure to a K rich aerosol is, in most cases, larger for promoted samples. This indicates that the increased Brønsted acidity provided by the WO₃ facilitates the transport of K in the catalysts, accelerating the poisoning.

Figure 1 shows the K concentration through a pair of three layer pellets which have been heat treated for 32 hours. While K has diffused into both of the un-doped 3%V₂O₅-7%WO₃/TiO₂ layers in one pellet, the alkaline MgO layer have completely hindered the transport of K in the other, indicating that K is more readily transported over acid sites.

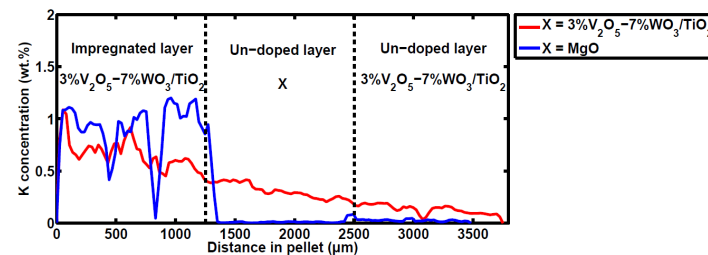


Figure 1. SEM-EDS measured K concentration profiles through three layer pellets heat treated at 350 °C in a flow of 6 vol.% O₂, 3 vol.% H₂O and balance N₂ for 32 hours.

Significance

Both the activity of K aerosol exposed SCR catalysts of varying composition as well as K concentration profiles through three layer pellets indicate that the potassium transport in V₂O₅ based catalysts is facilitated by acid sites.

References

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