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Basic investigation of the chemical deactivation of V_2O_5/WO_3-TiO_2 SCR catalysts by potassium, calcium, and phosphate

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The influence of the combustion products of different lubrication oil additives and impurities in fuel or urea solution on the activity and selectivity of V_2O_5/WO_3-TiO_2 catalysts in the selective catalytic reduction (SCR) of nitrogen oxides by ammonia was investigated. Focusing on the deactivation by calcium, phosphate, and potassium, the $DeNO_x$ activity followed the order $K \gg Ca > PO_4$. This trend was investigated on the structural level of the catalyst by means of temperature programmed desorption of ammonia (NH_3-TPD) and a DRIFT characterization of the adsorbed ammonia species. The results suggest that the studied elements strongly reduce the acidity of the SCR catalyst in the order $K \gg Ca > PO_4$ by mainly affecting the Brønsted acidity of the surface.

KEY WORDS: SCR catalyst; $DeNO_x$; deactivation effect; NH_3-adsorption; TPD; DRIFT.

1. Introduction

V_2O_5/WO_3-TiO_2 catalysts are widely employed for the selective catalytic reduction (SCR) of nitrogen oxides by ammonia in the flue gas from stationary sources and, recently, also from the exhaust gas of Diesel trucks, in which ammonia is substituted by harmless urea solution [1]. Vanadia is the active phase of this kind of catalyst. Tungsta is considered to as a promoter that stabilizes the anatase modification of titania, favors the spreading of the vanadia on the catalyst surface, and increases the acidity of the catalyst [2,3].

Over the lifetime of a heavy-duty Diesel vehicle equipped with an SCR system, a considerable amount of combustion products of different lubrication oil additives (Ca, Mg, Zn, P, B, Mo) and impurities in the fuel (e.g. K from raps methyl ester) or the urea solution (Ca, K) are deposited on the surface of the V_2O_5/WO_3-TiO_2 catalyst, thereby affecting its activity and selectivity. The deactivating effect of alkali and alkaline-earth metal oxides as well as phosphates has already been discovered long time ago, because these components are also present in the flue gas of fossil fuel power plants. In some studies on tungsta-free SCR catalysts, this deactivation is explained by the decreasing acidity of the catalysts [4,5]. However, very few studies were performed on tungsta-containing catalysts and no investigation is known to us, dealing with the chemical deactivation of SCR catalysts in Diesel vehicles. In the present paper we focus on preliminary results about the deactivation effect of calcium, phosphate and potassium on V_2O_5/WO_3-TiO_2 catalysts for Diesel SCR systems.

2. Experimental

2.1. Sample preparation

Metal substrates (400 cpsi, V = 7.2 cm^3) coated with 1.3 g V_2O_5/WO_3-TiO_2 each by Wacker-Chemie GmbH were impregnated at the Paul Scherrer Institute with water soluble compounds of the elements Ca, P, Zn, B, S, Mo and K and combinations thereof. The total loading of these elements was 0.4 mol%. In order to achieve a homogenous distribution of the elements in the catalytic coating, the monoliths were immersed for 2 s in the aqueous solutions of the different compounds. Then, the wet samples were dried in air at 90 °C and finally calcined for 5 h at 400 °C in order to initiate solid state reactions similar to the processes in the exhaust gas duct.

Two powder samples were prepared by pore-volume impregnation of a commercial V_2O_3/WO_3-TiO_2 SCR catalyst (Wacker-Chemie GmbH) with an aqueous solution of 10.5 mg/mL $Ca(Ac)_2$ (Merck GmbH), or 4.34 mg/mL K_2CO_3 (Fluka), respectively. The wet powders were dried for 12 h at 120 °C, and finally for 5 h at 550 °C. The resulting samples contained 0.18 wt% Ca or 0.18 wt% K, respectively, as resulted from the elemental analysis.

2.2. Catalytic activity

The coated catalyst modules were tested in a laboratory reactor with model gases (10% O_2, 5% H_2O, 1000 ppm NO, and 0–2000 ppm NH_3) at a GHSV of 52'000 h^{-1} in order to mimic typical conditions in a heavy-duty Diesel SCR system. The set-up has been previously described in detail [6]. The gases at the reactor outlet were continuously analyzed by means of an FTIR spectrometer (Nicolet Magna IR 560) equipped

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with a heated multiple-pass gas cell (Graseby Specac G-2-4-BA-AU, path length 2 m) and a mercury CdTe detector cooled by liquid nitrogen.

2.3. Temperature Programmed Desorption of NH_3 and DRIFT experiments

Temperature Programmed Desorption of ammonia (NH_3-TPD) was carried out by means of a Thermo TPDRO 1100 instrument, equipped with a TCD detector. About 0.2 g of powder catalyst were oxidized in a quartz tubular fixed reactor by a stream of 10% O_2 in He (20 mL/min) while heating up to 500 °C at 30 °C/min. After a hold time of 5 min the sample was cooled down to 50 °C and saturated with a gas mixture of 5% NH_3 in N_2 for 15 min. At the end of the saturation process, the sample was flushed with pure He at 20 mL/min until the TCD signal was stabilized. Then, the sample was heated up to 525 °C (ramp 10 °C/min) for 10 min. After the measurement the sample was cooled down in He and reoxidized. The adsorption and desorption cycles were repeated at 100, 150, and 200 °C.

DRIFT investigations were performed with a Nicolet Nexus 670 FTIR spectrometer, equipped with a DRIFT cell. Prior to NH_3 adsorption, the sample was dried *in situ* under a N_2 flow for 2 h at 250 °C. The sample was saturated at ambient conditions with 1000 ppm NH_3 in N_2 gas-mixture for about 30 min, and, then, flushed with N_2 for 1 h. Drift spectra were collected while heating up to 450 °C. The spectra of the adsorbed species were obtained by subtracting the contribution of the dried catalyst from the ammonia-covered sample.

3. Results and discussion

3.1. $DeNO_x$ activity

Figure 1a shows the $DeNO_x$ activity at 10 ppm of ammonia slip for differently poisoned V_2O_5/WO_3-TiO_2 catalysts coated on metal substrates. As expected, the fresh catalyst showed the highest NO_x conversion in the temperature range between 200 and 450 °C, and reached a plateau at about 350 °C. At this temperature, the $DeNO_x$ activity was about 100%. The presence of phosphate in the catalyst showed a slight deactivation effect at lower temperature. However, between 350 and 400 °C, the activity is still very high, and started to decrease at 400 °C. Calcium caused a strong reduction of the SCR activity, e.g. at 400 °C a maximum activity of only about 65% could be reached. It has to be noted that the deactivation by calcium was negligible when anions from inorganic acids ($SO_4^{2-} > PO_4^{3-} > BO_3^{-}$) were also present. Zinc was considerably less deactivating than calcium, but the effect of these anions in the Zn-containing sample was not as positive as in the case of the Ca-containing sample. Potassium caused a drastic deactivation of the fresh catalyst, resulting in less than 10% of NO_x conversion at 250 °C. In order to assess the maximum allowable potassium loading that could only moderately give rise to deactivation two additional catalysts containing 0.2 and 0.1 mol% of potassium have been prepared (figure 1b). The sample containing 0.2 mol% K showed a much higher SCR activity at lower temperature. However, at 450 °C this sample showed only about 25% of the $DeNO_x$ activity obtained for the fresh catalyst. Only for the 0.1 mol% K containing sample moderate deactivation was observed over the entire temperature range. The deactivation effect of different elements and combinations thereof are summarized in Table 1.

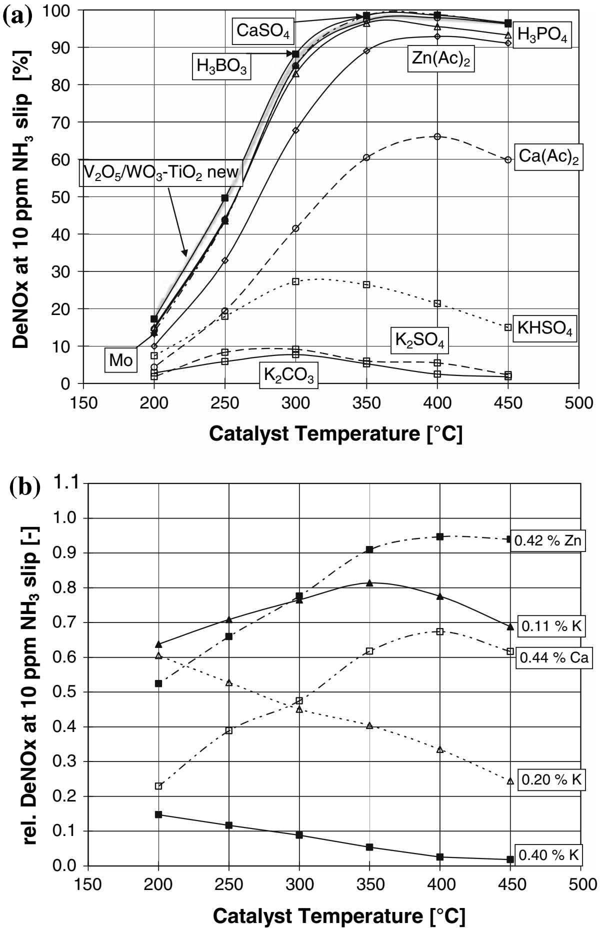

Figure 1. $DeNO_x$ activity of the poisoned and fresh V_2O_5/WO_3-TiO_2 SCR catalyst measured at 10 ppm NH_3 slip. (**a**) Influence of poisoning agents. (**b**) Influence of the potassium concentration in comparison to the Zn- and Ca-containing catalysts, given as reference samples.

The degree of N_2O production at T > 500 °C, which is typical for V_2O_5/WO_3-TiO_2 catalysts, was not influenced by the different compounds, except for molybdenum, which induced a small increase in N_2O formation.

The deactivation experiments were repeated with V_2O_5/WO_3-TiO_2 powder samples containing the selected elements potassium, calcium, and phosphate, in order to correlate catalytic results and detailed characterization data obtained for these samples.

Table 1
Deactivation potential of different poisoning agents and combinations thereof on the SCR activity of V_2O_5/WO_3-TiO_2, and the influence of increasing amounts of K only (last column)

Relative $DeNO_x$ at 10 ppm NH_3 slip	Element (containing 0.4 mol%, based on catalyst; ≈20 mol%, based on vanadium)					Influence of increasing amounts of K
>95% moderate deactivation	P	B	$CaSO_4$	Mo	P/B	
75–85%	Zn	Zn/P	Zn/B	Ca/P		K (0.1 mol%)
40–70%	Ca	Ca/B	Zn/$CaSO_4$			K (0.2 mol%)
20–40%	Ca/Zn	K/$CaSO_4$				
<20% strong deactivation	K	K/P	K/B	K/Zn	K/Ca	K (0.4 mol%)

3.2. NH_3-TPD

One of the most important steps of the SCR process is the adsorption of ammonia on the surface of the catalyst. Therefore, the SCR yield strongly depends on the acidity of the catalyst. In order to investigate the effect of deactivating agents on the acidity of the catalyst, we performed NH_3 TPD experiments. Figure 2 shows the NH_3 TPD curves of the fresh, calcium, and potassium containing catalysts, obtained in the range 100–525 °C. The evolution of ammonia occurred in a wide temperature range, due to the presence of adsorbed ammonia species with different thermal stability. All curves exhibit two peaks corresponding to weakly and strongly bound ammonia. When performing the ammonia adsorption at 100 °C, a large ammonia evolution was observed between 100 and 200 °C for all samples. It is noteworthy that the ammonia evolution in this temperature range was similar for both the fresh and the potassium containing sample, but significantly higher than that of the calcium containing sample. However, in case of the potassium containing sample, the ammonia evolution showed less tailing than that of the fresh sample, indicating that the weakly adsorbed ammonia species are more similar to those formed on the potassium containing catalyst.

At higher temperatures (200–300 °C), similar amounts of ammonia evolved from the potassium- and calcium-containing samples, but much less than from the fresh sample. In case of the calcium-containing sample, the ammonia desorption was complete at around 450 °C, whereas for the potassium-containing sample, ammonia fully desorbed only between 400 and 450 °C. These results are in good agreement with the $DeNO_x$ activity trend observed for these samples and shown in figure 1.

3.3. DRIFT characterization of the adsorbed NH_3 species

DRIFT spectroscopy was employed to elucidate the influence of potassium and calcium on the stability of the adsorbed ammonia species.

Figure 3A and B show the differential spectra of the adsorbed ammonia species on the fresh and on the potassium-containing catalysts respectively. The region between 1300 and 1700 cm^{-1} shows the features of two types of adsorbed species. The bands at 1425 and at 1670 cm^{-1} arise from the asymmetric and symmetric

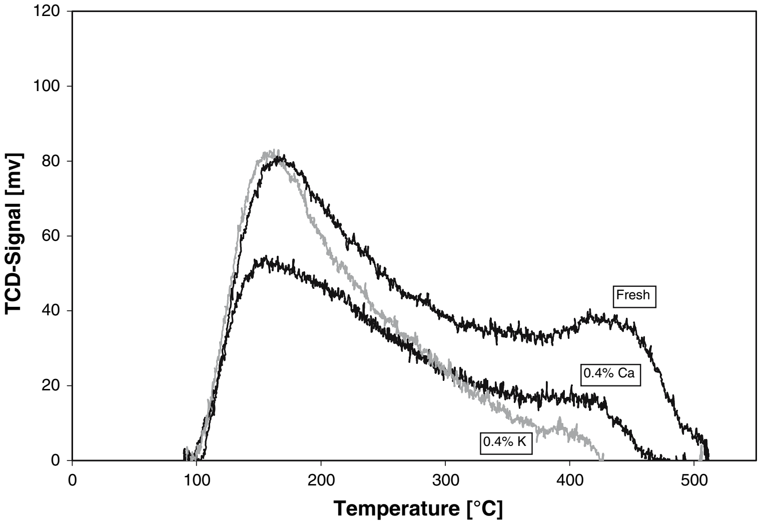

Figure 2. NH_3 TPD curve of the fresh, calcium-, and potassium-containing catalyst.

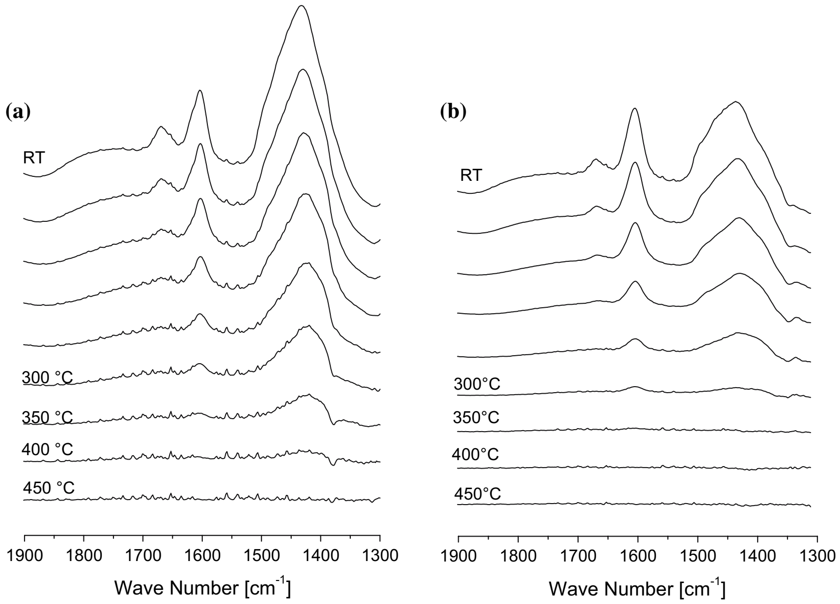

Figure 3. DRIFT spectra of adsorbed NH_3 species on the (**a**) fresh catalyst and (**b**) on the potassium-containing catalyst from RT to 450 °C.

deformation modes of ammonium ions respectively, which occur upon ammonia protonation on Brønsted acid sites. Whereas the sharp band at 1605 cm^{-1} is associated with the asymmetric deformation mode of ammonia species coordinated on Lewis acid sites [7,8]. Figure 3A shows that these bands slowly vanish upon heating, until all ammonia species are desorbed from the fresh catalyst at around 450 °C.

Figure 3B shows that for the potassium containing sample similar spectra are observed. However, on closer examination of the peaks at 1425 cm^{-1} and 1605 cm^{-1}, corresponding to the asymmetric deformation vibration of ammonia on Brønsted and Lewis acid sites respectively, it is easily discernible that in the case of the fresh catalyst the peak at 1425 cm^{-1} is more intense than that at 1605 cm^{-1}, whereas in the presence of potassium these signals showed comparable low intensities. This result indicates that potassium strongly affects the formation of the ammonium ion, as formed by adsorption of ammonia on the Brønsted acid sites. Moreover, in the presence of potassium the ammonia desorption was complete at 350 °C. The calcium-containing sample (not shown here) showed an intermediate behavior, i.e. the signals for the ammonium ions vanished at around 400 °C.

These results are strongly correlated to both the catalytic activity and the NH_3 TDP experiments and suggest that the deactivating elements strongly influence the Brønsted acidity of the SCR-catalysts. Chen *et al.* identified the V-OH groups of polymeric V_2O_5 as the active sites of this kind of catalyst. Moreover, they attributed the strong poisoning effect of alkali metals to their basicity, which causes the decrease of the Brønsted acidity of the catalyst [4], and thus the ability to store NH_3. Our results strongly support this mechanism.

4. Conclusions

The catalytic and spectroscopic results suggest that small amounts of potassium and calcium strongly reduce the surface acidity, and especially the Brønsted acidity of V_2O_5/WO_3-TiO_2 catalysts, thereby also decreasing their SCR activity. DRIFT characterization of the adsorbed ammonia species suggests that these elements strongly affect the Brønsted acidity of the catalyst surface, thus affecting the catalytic activity. Further characterization experiments are in progress in order to better understand the deactivation mechanisms induced by potassium, calcium, and other poisoning elements.

Acknowledgments

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References

[1] H. Bosch and F. Janssen, Catal. Today 2 (1998) 369.
[2] G.T. Went, L.J. Leu and A.T. Bell, J. Catal. 134 (1992) 479.
[3] J.P. Chen and R.T. Yang, Appl. Catal. A 80 (1992) 135.
[4] J.P. Chen and R.T. Yang, J. Catal. 125 (1990) 411.
[5] L. Lietti and P. Forzatti, Appl. Catal. B 3 (1993) 13.
[6] M. Kleemann, M. Elsener, K. Koebel and A. Wokaun, Appl. Catal. B 27 (2000) 231.
[7] A.A. Tsyganenko, D.V. Pozdnyakov and V.N. Filimonov, J. Mol. Struct. 29 (1975) 299.
[8] G. Ramis, G. Busca, F. Bregani and P. Forzatti, Appl. Catal. 64 (1990) 259.