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# Sulfate Promoted Zirconia as Promising Alkali-Resistant Support for Catalytic NO<sub>x</sub> Removal

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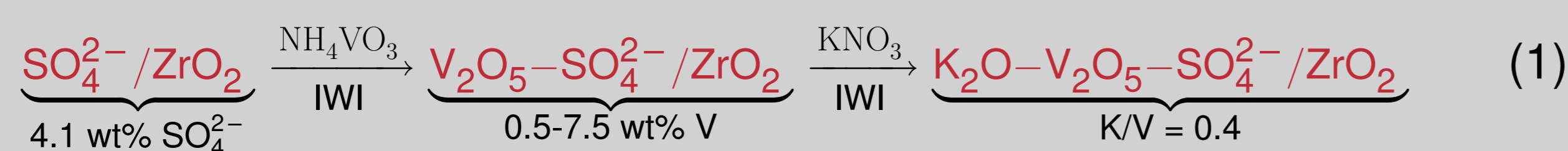
## 1. Introduction

THE use of bio-fuels as alternatives to traditional fossil fuels has attracted much attention recent years since bio-fuels belong to a family of renewable types of energy sources and do not contribute to the green-house effect. Selective catalytic reduction (SCR) of NO<sub>x</sub> with ammonia as reductant is the most efficient method to eliminate NO<sub>x</sub> from flue gases in stationary sources.

The traditional SCR catalyst suffers significant deactivation with time due to the presence of relative large amounts of potassium in bio-fuels. A possible solution to this problem is use of highly acidic supports, which would interact with potassium stronger than active metal species.<sup>[1,2]</sup>

## 2. Experimental

THE sample of sulfated zirconia with 4.1 wt% sulfate has been obtained commercially. The as-received support was impregnated with ammonium metavanadate via incipient wetness impregnation and calcined in air at 400°C, resulting in 0.5-7.5 wt% vanadium with a BET surface area of 145 m<sup>2</sup>/g. The vanadia-based catalysts were impregnated with 130 μmol/g KNO<sub>3</sub>.

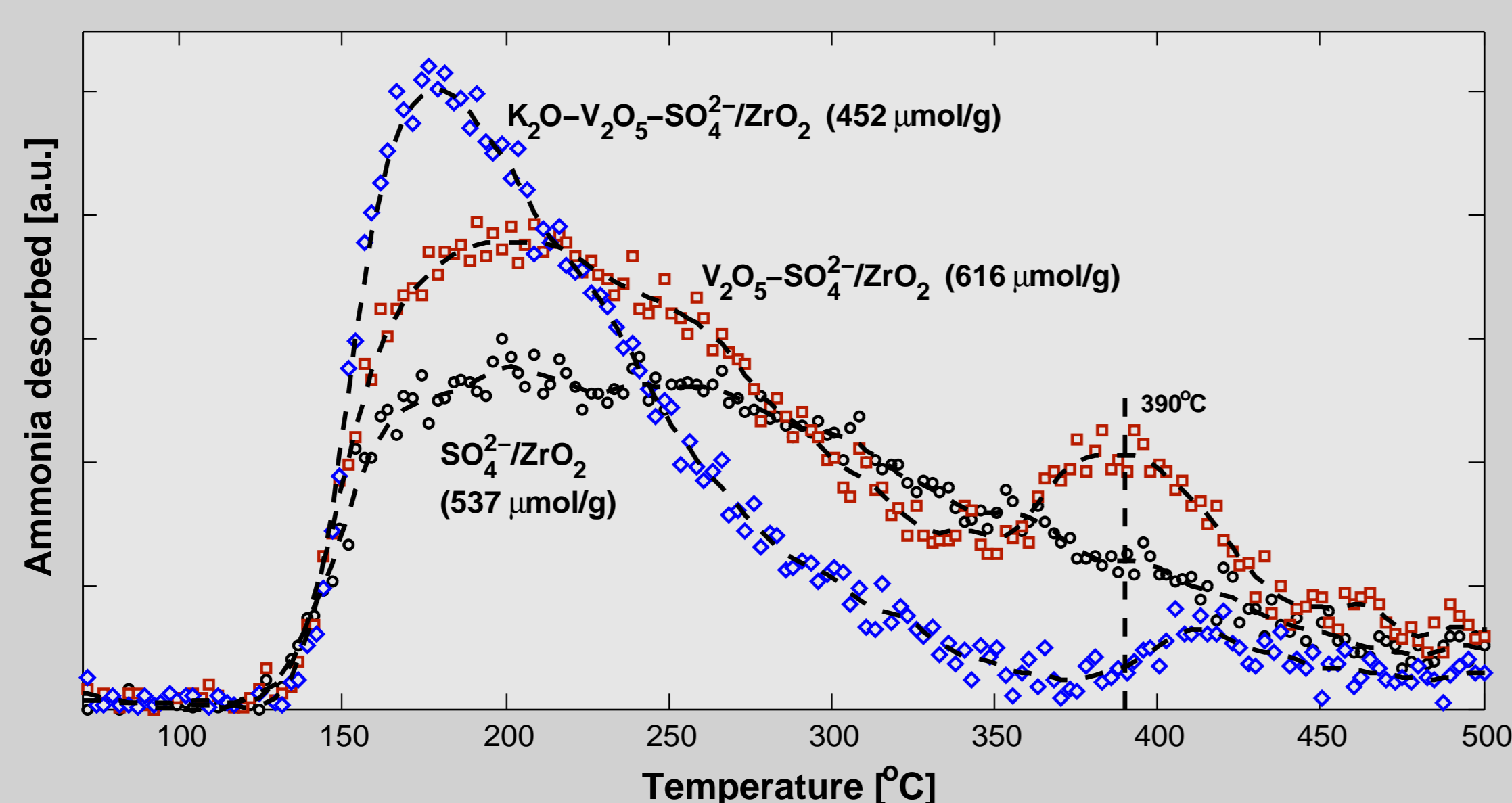


A 3%V<sub>2</sub>O<sub>5</sub>-7%WO<sub>3</sub>/TiO<sub>2</sub> catalyst with a BET surface area of 61 m<sup>2</sup>/g was used as a reference.

NO SCR was performed with 50 mg sample in 1000 ppm NO, 1100 ppm NH<sub>3</sub>, 3.5% O<sub>2</sub>, and 2.5% H<sub>2</sub>O, balanced with N<sub>2</sub>, total flow: 300 ml/min.

## 3. Sample Acidity

IMPREGNATION of the sulfated zirconia with vanadia results in an additional ammonia desorption peak around 390°C (Fig. 1). This peak is only observed in vanadia-containing samples on sulfated zirconia and not i.e. in tungstated zirconia<sup>[1]</sup>.

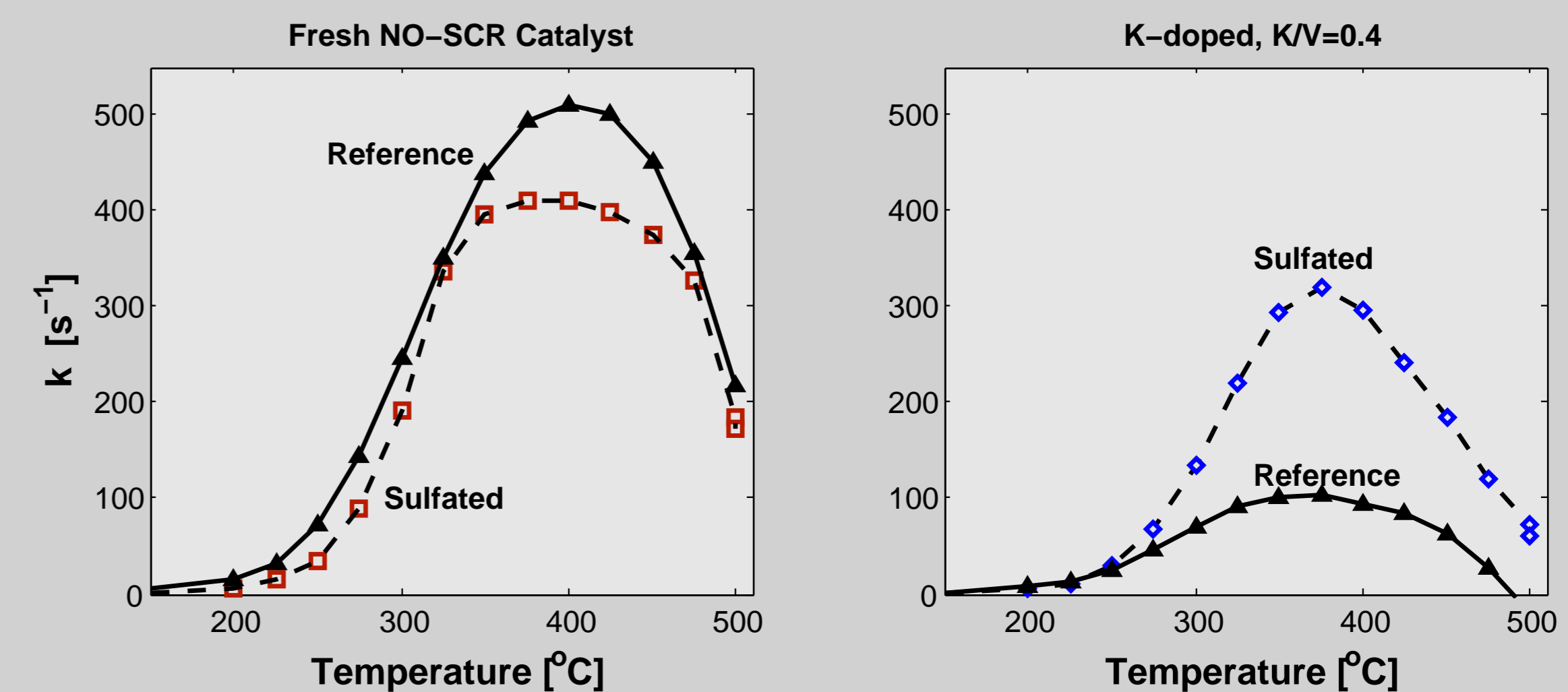


**Figure 1:** NH<sub>3</sub>-TPD of the sulfated samples (Surface acidity in brackets), indicating a formation of a stronger acid site with addition of 1.7 wt% V

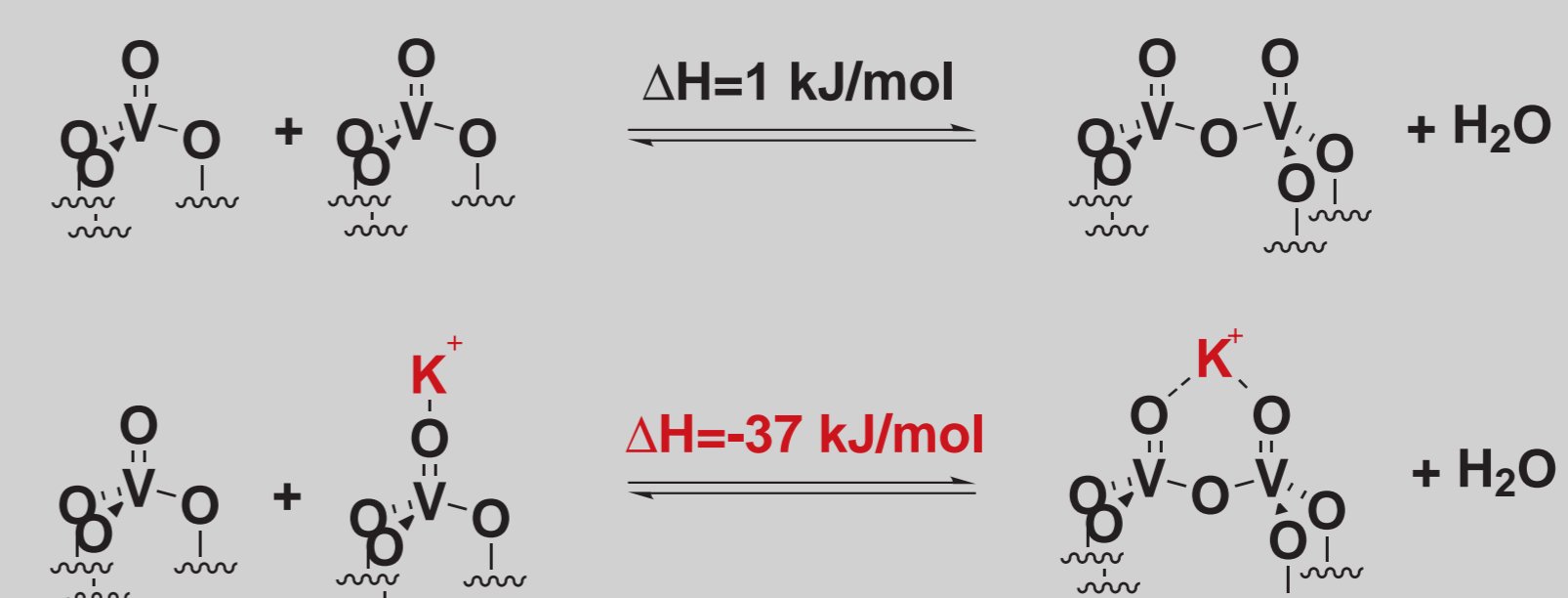
## 4. NO SCR Activity

CATALYSTS based on sulfated zirconia exhibit good SCR properties compared with the titania-based reference catalyst, both depicted in Fig. 2. Especially the SCR activity after K-doping reveals the high alkali resistance of sulfated supports over the traditional catalyst, the latter deactivating 71% at 300°C, whereas the sulfated catalyst only deactivates 29%.

Optimization of the vanadia loading was performed to study the catalysts resistance toward a constant amount of potassium (130 μmol/g). The deactivation of catalysts containing 0.5–7.5 wt% vanadium due to potassium poisoning is depicted in Fig. 4, top.

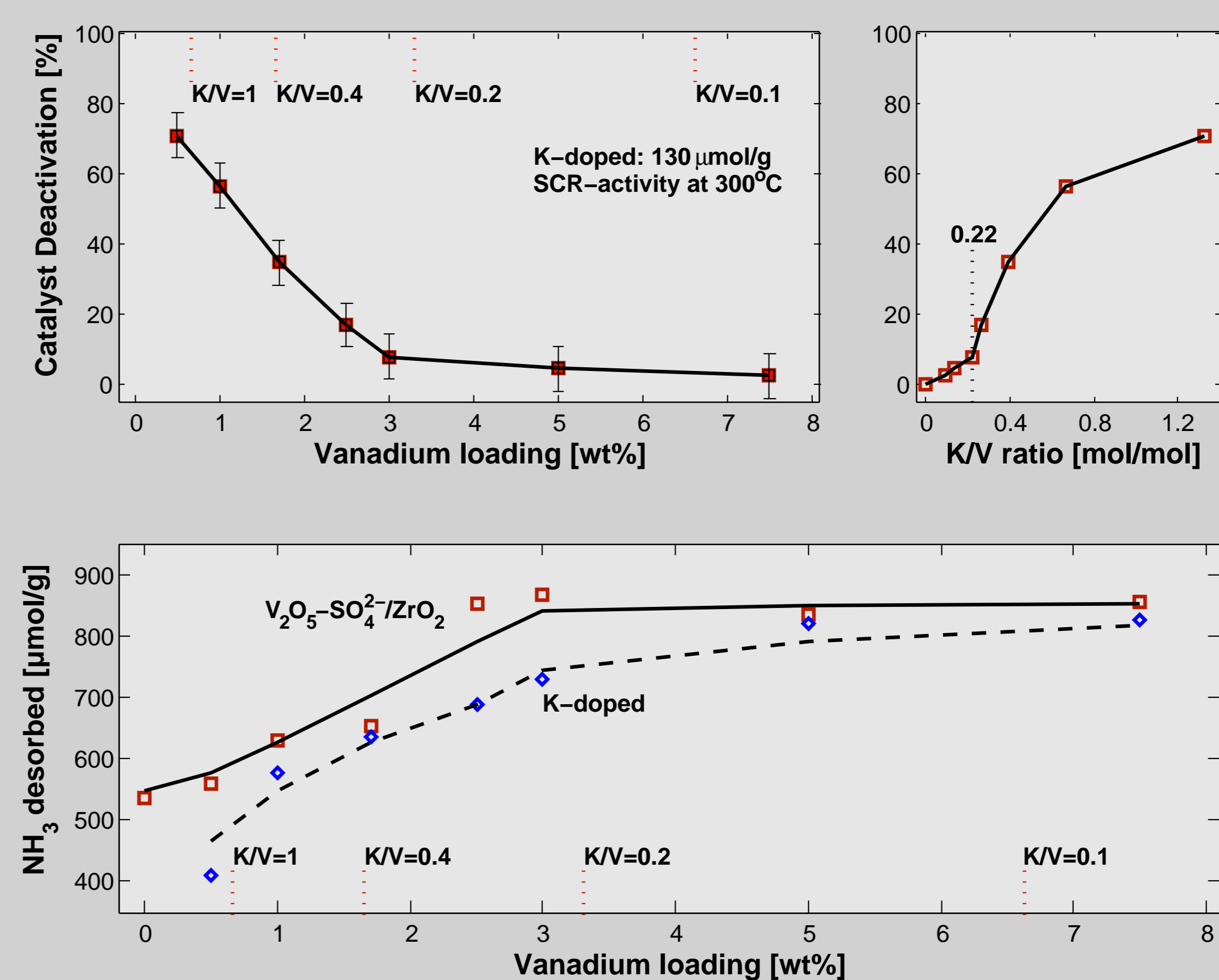


**Figure 2:** The temperature dependency of the SCR activity of 3wt% V<sub>2</sub>O<sub>5</sub>-4.1wt% SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and a 3 wt% V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> reference catalyst



**Figure 3:** The propensity for dimerization calculated by DFT. Notice with potassium present, the dimer is now clearly favored in enthalpy<sup>[3]</sup>

Increasing the amount of vanadium, thus decreasing the K/V ratio, results in significant decrease in catalyst deactivation (Fig. 4, top left). At K/V = 0.2 only about 10% catalyst deactivation is observed, which even decreased further with increasing vanadium concentration.



**Figure 4:** Top left: Catalyst deactivation with different vanadia loadings at 300°C; Top right: Deactivation versus the K/V molar ratio, with threshold at K/V = 0.22; Bottom: Amount of desorbed NH<sub>3</sub> from the vanadia-impregnated support and the corresponding K-doped samples

## 5. Conclusion

CATALYSTS based on sulfated zirconia show good resistance towards potassium poisoning. For samples with K/V ratios below 0.22, potassium seems to have very low impact on the catalysts performance.

Poisoning the catalysts with potassium mainly affects the strong acid sites, with NH<sub>3</sub> desorption temperature around 390°C.

## References

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- [2] Kustov, A.L., Kustova, M.Y., Fehrmann, R., Simonsen, P., *Appl. Catal. B*, 58 (2005) 97–104.
- [3] Due-Hansen, J., Boghosian, S., Kustov, A.L., Frstrup, P., Tsilomelekis, G., Ståhl, K., Christensen, C.H., Fehrmann, R., *J. Catal.*, submitted, april 2007.