Sulfated Zirconia as Alkali-Resistant Support for Catalytic NO_x Removal

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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_x with ammonia as reductant is the most efficient method to eliminate NO_x from flue gases in stationary sources. The traditional SCR catalyst suffers significant deactivation with time due to the presence of larger amounts of potassium in bio-fuels. A possible solution of this problem is use of highly acidic supports which would interact with potassium stronger than active metal species [1, 2]. Among potential carriers, sulfated zirconia is of high interest because its acidic and textural properties can be modified by varying preparation conditions [3].

Materials and Methods

The samples of sulfated zirconia with different sulfate loading have been obtained commercially. The as-received supports were impregnated with ammonium metavanadate via incipient wetness method and calcined in air at 400˚C, resulting in 3.0 wt% V_2O_5 (1.7 wt% V). Subsequently, the vanadia-impregnated catalysts were doped with potassium to obtain a K/V molar ratio of 0.4 followed by drying at 100˚C.

The samples were characterized by X-ray powder diffraction, BET surface area, temperature programmed desorption of ammonia (NH_3-TPD), and NO-SCR measurements. The concentration of acid sites (sites to which ammonia is adsorbed during NH_3-TPD) is calculated from the ratio between the amount of ammonia desorbed and BET surface area. NO-SCR is performed with 75 mg sample and reaction mixture containing: 1000 ppm NO, 1100 ppm NH_3, 3.5% O_2 and 2.5% H_2O, total flow 300 ml/min, balanced with N_2.

Results and Discussion

The properties of the catalysts based on sulfated zirconia supports with different sulfate concentration are summarized in table 1. All commercial samples reveal high surface area and crystallinity which decrease with the increase of the sulfate loading. Combining the results of NH_3-TPD and BET measurements, it is possible to estimate the concentration of acid sites, which is a useful parameter, determining the resistance of the samples towards poisoning with potassium [2].

The catalytic performance of the samples based on sulfated zirconia is presented in Fig. 1. The results are compared with a reference catalyst 3 wt% V_2O_5-7 wt% WO_3/TiO_2, (1.7V_6WT), representing the traditional SCR catalyst. The catalysts supported on sulfated zirconia show high initial activity comparable to that of the reference catalyst. After doping with potassium, the sulfated catalysts display superior resistance towards poisoning; 1.7V_3SZ catalyst loose only 29% of the initial activity at 300˚C, whereas the reference catalyst deactivates 71%.

Table 1. Physical-chemical characteristics of the catalysts.

Catalyst	SO_3 conc.*	BET area*	Acid conc.*	Crystal-linity*	Deactivation†	Remaining Activity†
	wt%	m^2/g	μmol/m^2	%	%	s^{-1}
1.7V_3SZ	3.4	145	3.7	73	29	104
1.7V_4SZ	3.9	130	2.4	60	38	41
1.7V_5SZ	4.9	125	3.9	53	31	12
1.7V_6WT	-	68			71	59

*measured for the support, † at 300˚C

Even though samples based on sulfated zirconia are much less affected by the poisoning with potassium, the deactivation is still quite severe. This indicates that potassium is eventually distributed between the acid sites of the support and active vanadia species.

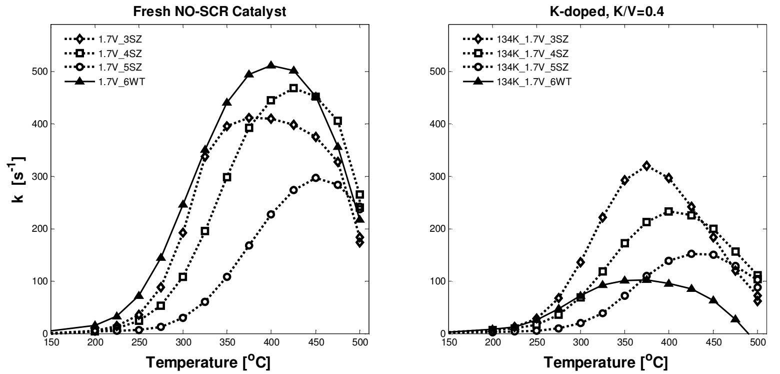

Figure 1. Temperature dependency of the first-order rate constant for the fresh catalysts (left) and the corresponding potassium-doped catalysts (right).

Significance

SCR catalysts based on sulfated zirconia show improved resistance towards potassium poisoning and can therefore be applied to a higher extent in power plants utilizing alkali rich biomass without compromising the emission of NO_x due to catalyst deactivation.

References

1. Kustov, A.L., Kustova, M.Y., Fehrmann, R., and Simonsen, P., *Appl. Catal. B*, 58, 97 (2005).
2. Due-Hansen, J., Kustov, A.L., Rasmussen, S.B., Fehrmann, R., and Christensen, C.H., *Appl. Catal. B*, 66, 160 (2006).
3. Arata, K., *Appl. Catal. A*, 146, 3 (1996).