Diffusion Limitations and Effectiveness Factor of Mesoporous and Hierarchically Structured Catalysts for SCR-DeNO$_x$

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Due to stricter environmental regulations for minimizing NO_x emissions, the urge to apply efficient catalysts is a worldwide concern. Among the technologies for controlling NO_x-emissions, the selective catalytic reduction of NO_x (SCR-DeNO$_x$) is the main industrial application. Vanadia supported on mesoporous titania is the most common catalyst wash-coated on SCR monoliths [1]. Such wash-coats lack a well-defined pore architecture, which leads to diffusion limitations and compromised material use. Theoretical studies have shown that by introducing macropores in a conventional SCR catalyst, its efficiency can be increased by up to 180% [2]. However, a direct proof of the effect of pore hierarchy on the catalytic activity of SCR-DeNO$_x$ reaction is lacking.

In order to experimentally investigate the effect of additional macropores in a SCR catalysts, mesoporous and hierarchically structured (meso-/macroporous) V_2O_5/TiO_2 mixed oxides with different V_2O_5-contents (1, 3.5 and 5 wt.%) were prepared via a modified sol-gel method [3]. Characterization results show that the catalysts have similar content and nature of V_2O_5-species, independent of their pore architecture. The diffusion effect on the catalytic activity was measured for a mesoporous catalyst by varying its grain size. By using the Weisz-Prater criterion to estimate the Thiele modulus and the effectiveness factor from the observed reaction rates, diffusion limitations were indeed found for the DeNO$_x$ reaction (ϕ~3 and η~0.7) for $\bar{d}_{cat.grain}$= 0.25 mm (Figure 1). The results from SCR of NO with NH_3 ($m_{cat.}$= 0.2 g, $\bar{d}_{cat.grain}$ = 0.25 mm, T = 423− 773 K, GHSV = 21.300 h^{-1}, n(NO)/n(NH_3) = 2/1) over mesoporous and hierarchical V_2O_5/TiO_2 catalysts show that NO conversion increases with V_2O_5-content. However, the hierarchical catalysts exhibit a higher overall reaction rate over the whole temperature range (T_R = 423− 773 K) when compared to their mesoporous counterparts with same V_2O_5-content. The NO consumption rate (r_{NO}) increases by up to 200%, and the light-off temperature ($T_{Light-off}$) decreases by 50 K when additional macropores are present (Figure 2). Considering the surface properties of the materials and the fact that DeNO$_x$ is limited by intraparticle diffusion, the higher activity of the meso-/macroporous catalysts (for the same V_2O_5 content) can be attributed to diffusion facilitation within the catalyst particle. These results provide the first experimental proof of the advantage of pore hierarchy in SCR-DeNO$_x$ as predicted earlier from theoretical calculations [2].

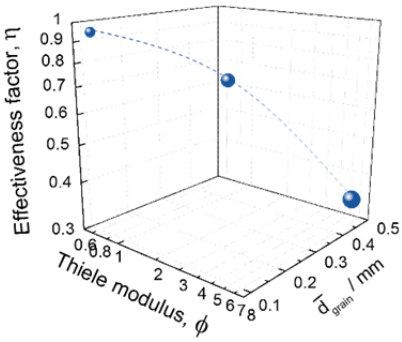

Figure 1: Effectiveness factor and Thiele modulus for different grain sizes of the 5 wt.% V_2O_5/TiO_2 mesoporous catalyst.

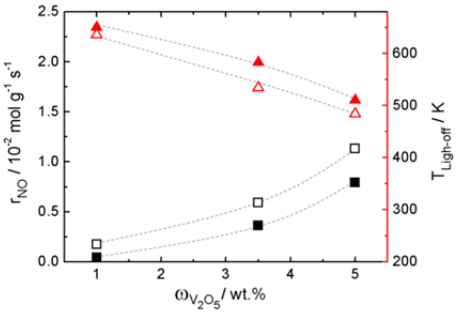

Figure 2: Reaction rate (r_{NO}) at 523 K and light-off temperature ($T_{Light-off}$) during SCR-DeNO$_x$ over mesoporous and hierarchical V_2O_5/TiO_2 catalysts with different V_2O_5-content.

References

[1] P. Forzatti: *Present status and perspectives in de-NOx SCR catalysis.* Appl. Catal. A. **222**, 221-236 (2001).

[2] G. Wang, M.-O. Coppens: *Calculation of the optimal macropore size in nanoporous catalysts and its application to DeNO(x) catalysis*. Ind. Eng. Chem. Res. **47**, 3847-3855 (2008).

[3] G. Hasegawa. K. Kanamori, K. Nakanishi, T. Hanada: *Facile Preparation of Hierarchically Porous TiO_2 Monoliths*. J. Am. Cer. Soc. **93**, 3110-3115 (2010).