Fundamental deactivation and regeneration mechanisms of Fe-BEA as catalyst for selective reduction of nitrogen oxides in oxygen excess

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Introduction

Selective catalytic reduction with ammonia (NH_3-SCR) is a well-established and effective method to eliminate nitrogen oxides (NO_x) in oxygen excess for stationary and, more recently, also for mobile applications [1]. For the latter case, metal exchanged zeolites are attractive alternatives to vanadia-based SCR catalysts. However, several challenges arise when using these materials in exhaust gas aftertreatment systems for diesel and lean-burn vehicles. Two of the more important issues are the hydrothermal stability the tolerance against chemical poisoning of the metal exchanged zeolites [1].

This presentation will focus on iron-exchanged zeolite beta, Fe-BEA, as NH_3-SCR catalyst. The deactivation of Fe-BEA after hydrothermal treatment and phosphorous exposure has been studied experimentally and by kinetic modeling as well as regeneration of the catalyst using hydrogen treatment. The fundamental mechanisms for thermal and chemical degradation of Fe-BEA will be presented and discussed together with regeneration of the catalyst by hydrogen exposure.

Materials and Methods

Cordierite supported Fe-BEA samples were prepared and thermally and chemically deactivated by exposing them to high-temperatures and phosphorous in a continuous flow reactor system [2,3]. Furthermore, hydrothermally treated Fe-BEA was further exposed to hydrogen [4]. The samples were characterized with DRIFTS, BET, XPS, XRD, NH_3-TPD and UV-Vis. The catalytic performance of the samples for NH_3-SCR, and NO and NH_3 oxidation was studied by steady state and transient flow reactor experiments. Based on the experimental results, a kinetic model was developed to describe the kinetics and the fundamental deactivation mechanisms for Fe-BEA with focus on the dynamics of the active iron sites [2].

Results and Discussion

The mechanisms for thermal deactivation, chemical deactivation due to phosphorous exposure and regeneration after high-temperature hydrogen treatment of Fe-BEA are schematically summarized in the Figure. The hydrothermal treatment results of Fe-BEA can be divided into two parts; (i) milder ageing results in a decreased amount of isolated iron species, forming oligomeric iron clusters in the zeolite pores, and (ii) more severe ageing results in continuous migration and formation of larger iron oxide particles located on the external surface of the zeolite. This change in the nature of the active iron species results in lower NH_3-SCR activity. Furthermore, exposure of Fe-BEA to a relatively low amount of phosphorous results in formation of metaphosphates blocking active iron species and hence chemical deactivation of the SCR catalyst. The Fe-BEA catalyst can partially be regenerated by high-temperature exposure to hydrogen, re-dispersing larger iron species to active monomeric and dimeric iron species. The developed kinetic deactivation model describes the experiments well for both thermally and chemically deactivated samples. To simulate the deactivation process the number of active sites is decreased in the model to predict the effect of hydrothermal and chemical deactivation due to loss of active iron sites.

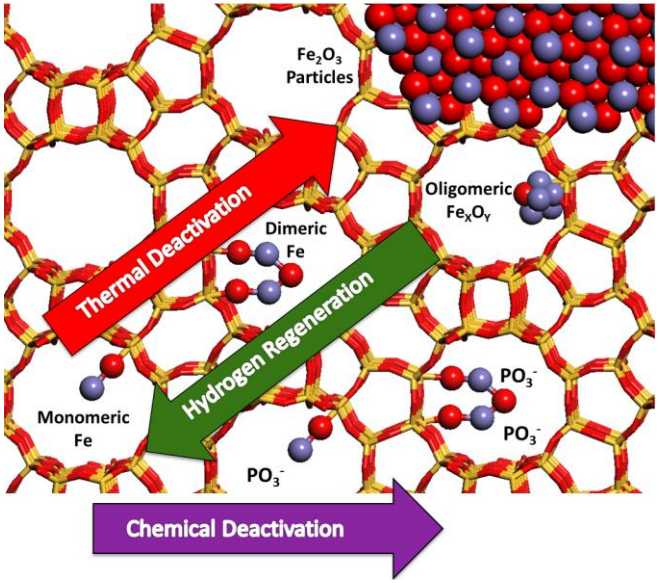

Figure: *The different mechanisms discussed in the presentation; thermal and chemical deactivation as well as hydrogen regeneration of Fe-BEA.*

Significance

Understanding catalyst deactivation mechanisms is very important for the choice of operation conditions for catalytic processes and for the design of new catalyst formulations. For mobile applications, catalyst deactivation is a practical concern in terms of sizing the catalyst for the lifetime of the vehicle and in accounting for performance loss over time for the catalyst. Our studies contribute to the understanding of the fundamental deactivation mechanisms of Fe-BEA as NH_3-SCR catalyst with focus on the active iron sites. The results show how the dynamics of the different active sites together with activity studies may be used to create kinetic deactivation models.

References

1. S. Brandenberger, et al., *Catal. Rev.-Sci. Eng.* 50 (**2008**) 492-531.
2. S. Shwan, et al., *Catal. Today* 197 (**2012**) 24-37.
3. S. Swan, et al., *Appl. Catal. B* 147 (**2014**) 111-123.
4. R. Nedyalkova, et al., *Appl. Catal. B* 138–139 (**2013**) 373-380.