

Study of a Zeolite-based system as NH₃-SCR catalyst for Diesel exhaust aftertreatment

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Introduction

Tightening NO_x emission standards for heavy-duty and passenger car engines require the development and application of highly efficient aftertreatment system. One technology already adopted for heavy duty application to comply with EURO 4 is the selective catalytic reduction (SCR) of NO_x with NH₃/urea [1]. Currently, commercial SCR catalysts are extruded monoliths made of a TiO₂ anatase carrier supporting the active components (i.e. V₂O₅, WO₃). However, a new class of catalysts is now being considered, as more active at low temperature; these catalysts are based on Zeolite systems, promoted with different transition metals (e.g. Cu, Fe), and they are used in the form of coated monoliths.

In this work the reactivity of a commercial Zeolite-based catalyst in the SCR reactions is analyzed and compared with that of a commercial vanadium-based catalyst [2].

Materials and Methods

Intrinsic kinetic experiments were performed under dynamic conditions in a flow-microreactor loaded with powdered catalyst obtained by grinding and sieving (140-200 mesh) either the original precursor washcoat powder (100 mg) or the commercial washcoated monolith catalyst (160 mg). The exit of the reactor was directly connected to a quadrupole mass spectrometer (Balzers QMS 200) and to a UV-analyzer (ABB LIMAS 11HV) in parallel for the analysis of gases. Typical feed gas composition was NH₃ (0-1000 ppm), NO_x (0-1000 ppm), O₂ (2-6% v/v), H₂O (1-10% v/v), at flow rates between 120-280 Ncc/min. Catalyst reactivity was studied in the temperature range 50-550°C [2,3]. The monolith samples (around 8 cm³ volume) were analysed under isothermal steady-state conditions within the range 150 – 450°C. Typical concentrations of NO_x and NH₃ were 500 - 1000 ppm, O₂ 2-10 % and water 1-10 % v/v. The space velocity was set to 36000h⁻¹ with nitrogen as balance. Analysis of gases was performed using a UV-analyzer (ABB LIMAS 11HV).

Results and Discussion

The kinetics of the NH₃ adsorption-desorption reaction were first investigated over the powder samples in the range of 50-200°C by step feed experiments followed by TPD. The results collected over the precursor powder showed a strong NH₃ adsorption on the Zeolite-based catalyst, together with the capacity to retain NH₃ up to high temperatures. The ammonia storage capacity measured over the crushed monolith was found to be lower (0.48 vs. 0.77 mol_{NH₃}/g_{active phase} @150°C) and different kinds of ammonia adsorbed species seems were apparently formed over the two systems. Indeed, during TPD runs complete ammonia desorption could be achieved within 500°C over the crushed monolith, while over the washcoat powder the desorption process was not yet completed at 550°C: this suggests that stronger ammonia adsorbed species are formed over the washcoat powder, which are stable up to higher temperatures. The comparison with data collected under identical experimental conditions over

a V-based commercial catalyst showed that in any case the vanadium catalyst was characterized by a lower capacity (0.20 mol_{NH₃}/g_{active phase} @150°C) [3]. Furthermore the zeolite catalysts were able to retain adsorbed ammonia species up to higher temperatures.

The ammonia oxidation reaction was then addressed: over both the zeolite washcoat powder and the zeolite crushed monolith it was found that the reaction occurred starting around 300°C with formation of nitrogen only, but different activities were measured. Indeed, a quantitative analysis of data indicated that the crushed monolith powder was about six times less active in NH₃ oxidation. Under similar conditions, over the vanadium based catalyst the reaction started around 380°C. Similar results were found in the analysis of the NO oxidation reaction: over both the powder samples the onset for NO₂ formation was around 150°C, but again the crushed monolith was found less active the washcoat powder (13% NO conversion at 450°C Vs 6% respectively). The same experiment performed on vanadium based catalyst showed no significant activity in NO oxidation.

Finally the standard SCR reaction was analyzed. Over both the powder samples, the SCR reaction was active already at 200°C: total NO and ammonia conversions were achieved around 380°C over washcoat powder and around 450°C over the crushed monolith, with formation of nitrogen only. The crushed monolith was roughly 2-3 times less active than the washcoat precursor powder: indeed, E_{act} estimates were close to 10 kcal/mol for both systems versus E_{act} 16 kcal/mol for the V-based catalyst [2,3].

Experimental runs were then performed over a small monolith sample in order to understand which of the powder samples was better representative of real catalyst. The results showed that the monolith sample was characterized by a deNO_x activity similar to that of the crushed monolith rather than that of the original washcoat powder. Another important information gained by the comparison between monolith and monolith crushed powder is that diffusional limitation do not seem to significantly affect the activity of the Zeolite system. When comparing the activity of the zeolite-based catalyst with that of the vanadium system assuming the same volumetric space velocity, the latter was found much more active than the zeolite system: this is related however to the fact that the vanadium catalyst is an extruded monolith while the zeolite monolith is washcoated, thus with a lower amount of active phase. But when comparing the results on the basis of the same flow rate per gram of catalyst, it appears that the two systems had similar activity at low temperature, while for T>300°C the zeolite system exhibited higher conversions.

Significance

The analysis of the set of the microreactor experiments performed over the zeolite system are preliminary to the development of the reaction kinetics and eventually of a chemically and physically –based, fully transient two-phase 1D+1D mathematical model of SCR honeycomb monolith converters. Numerical simulations are successfully used to optimized the performance of the different catalyst technologies under realistic transient operating conditions.

References

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