Hydrothermal aging effects on Cu-zeolite NH_3-SCR catalyst

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Introduction

After-treatment systems for Diesel vehicles face a challenge for upcoming emission regulations. Regarding the level of nitrogen oxides (NO_x) and soot required the global catalytic activity of the exhaust line needs to be improved. Conversion efficiency during cold-start and transient engine conditions needs to be clearly enhanced and the combination of deSoot and deNOx systems in series or in a same close-coupled device seems to be the most appropriate solution to beneficiate from the engine enthalpy. Nevertheless, the thermochemical conditions explored during particulate filter regeneration are very stringent for the catalyst and can strongly reduce its durability. Ammonia Selective Catalytic Reduction (NH_3-SCR) systems mainly based on Copper or Iron exchanged zeolite catalysts have emerged as effective technologies to reduce NO_x emissions, their durability being continuously improved.

In this work, we evaluated the impact of different hydrothermal treatments on a commercial copper-exchanged zeolite catalyst. The goal was to link the catalytic material modifications with catalytic performance changes as a function of both aging duration and temperature. The mechanism evolution of the zeolite structure as well as the changes of the copper state were experimentally investigated.

Materials and Methods

A commercial NH_3-SCR catalyst containing copper exchanged zeolite supported on a 400 cpsi (cells per square inch) cordierite honeycomb substrate was used in this study. Cylindrical samples of 1" diameter and 2" length were cored from a commercial copper-zeolite substrate. The samples were hydrothermally aged in a N_2 atmosphere containing 10% O_2 and 10% H_2O vapor injected at a flow rate of 5 liters/min. The aging was carried out in a muffle oven at 600°C for 2 hours, at 750°C for 16 hours and 64 hours, at 850°C for 4 hours, 16 hours and 64 hours, and at 950°C for 1 hour and 4 hours. The elementary composition of the active phase was characterized by X-ray Fluorescence (XRF). The zeolite structure and its evolution were determined by XRD and Si/Al ratio by 29Si MAS NMR.

The reactivity of the monolith cores was tested in a bench flow reactor system. The gas supply system was used to produce a synthetic gas mixture with a composition similar to a Diesel engine exhaust. The concentration of CO_2, O_2, NO, NO_2, N_2O and NH_3 was measured.

Results and Discussion

Figure 1A shows molecular nitrogen adsorption isotherms for different hydrothermal aging temperatures and durations. The fresh sample is composed of a large microporosity (0.162 cm^3/g) specific to the zeolite. Aging treatments lead to a loss of micropore volume and from treatment at 850°C for 4h a significant loss is observed. The local destruction of the zeolite framework induces micropores loss. Kharas et al. [1] assigned this framework destruction to copper sintering and dealumination, their conclusions are partially confirmed by XRD patterns combined with ^{27}Al MAS NMR. The crystallinity starts actually to decrease when about 20% of copper and almost 20% BET surface area is lost. This could indicate that the copper was somehow protecting the zeolite structure which is in accordance with the conclusions of Grinsted et al [2]. These authors confirmed the inhibiting effect of the Cu ions on the dealumination of ZSM-5 previously suggested by Suzuki et al [3].

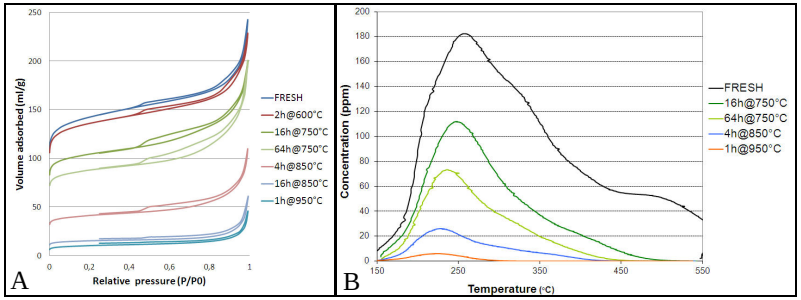

Figure 1. A) N_2 adsorption-desorption isotherms and B) NH_3-TPD curves of Cu-zeolite for different hydrothermal aging

Based on these experimental analysis, a global kinetic model of catalyst aging in hydrothermal conditions was developed. Its consistency was checked with NH_3-TPD experiments. As can be seen in **figure 1B**, the ammonia released during desorption decrease depends strongly on hydrothermal aging conditions. Ammonia can be adsorbed on three different forms on copper zeolite : on Brönsted acid sites to form NH_4^+, coordinated with Cu^{2+} Lewis sites to form $[Cu(NH_3)_x]^{2+}$ (with x= {1;2;3;4}) complexes and adsorbed on extra-framework aluminium (EFAl) species. The variation of the number of each adsorption site was evaluated using the hydrothermal aging model. By coupling these results to a kinetic model of NH_3 sorption adapted from our previous work [4], NH_3-TPD experiments can be well predicted.

Significance

Based on a detailed material properties analysis of Cu-zeolite, adsorption and desorption of NH_3 can be quantitatively predicted as a function of hydrothermal aging conditions. This work is a first step to bridge the gap between lab analysis conclusions and global reactivity observed in real conditions.

References

1. Kharas, K.C.C.; Kobota, H.J.; Liu, D.J. *Applied Catalys B Environmental*, *2*, 1993, 225.
2. Grinsted, R. A.; Jen, H. W.; Montreuil, C. N.; Rokosz, M. J. ; Shelef, M. *Zeolites* 13, 1993, 602.
3. Suzuki, K.; Sano, H.; Shoji, H.; Murakami, T.; Ikai, S.; Shin, S.; Hagiwara, H.; Takaya, H. *Chem. Lett.* 1987, 1507.
4. Skarlis, S.A.; Berthout, D.; Nicolle, A.; Dujardin, C.; Granger, P.; *J. Phys. Chem.C*, 2013, 117(14), 7154.