Impact of sulfur oxides on catalytic functions of Cu-SAPO-34

K. Wijayanti[1], S. Andonova[2], A. Kumar[2], J. Li[2], K. Kamasamudram[2], N.W. Currier[2], A. Yezerets[2], L. Olsson[1*]

[1]*Competence Centre for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden*

[2]*Cummins Inc., 1900 McKinley Ave, MC 50183, Columbus, IN 47201, USA*

**louise.olsson@chalmers.se*

Introduction

Ammonia SCR is an efficient method for reducing NO_x from stationary sources as well as from vehicles operated in lean environment. Copper exchanged small pore zeolites, Cu-SAPO-34 and Cu-SSZ-13, were proven to be very active and showed robust performance even after extreme hydrothermal aging. On the other hand oxides of sulfur, ubiquitous in the diesel engine exhaust, is expected to decrease the catalyst performance [1]. In this study, the findings on SO_2 interaction with Cu-SAPO-34 and its impact on various catalytic reactions relevant for the SCR mechanism will be presented.

Materials and Methods

The SAPO-34 zeolite was synthesized and copper was introduced using aqueous exchange method in two steps, first with NH_4NO_3 in two stages followed by $Cu(NO_3)_2$. After drying and calcination, the Cu-SAPO-34 obtained was coated on cordierite monolithic substrate using incipient wetness method. Moreover ICP-AES, BET surface area and XRD analysis were conducted. The heat of adsorption of SO_2 on Cu-SAPO-34 was determined by microcalorimeter measurements.

Flow reactor experiments were performed using 3,500 mL min^{-1} total flow resulting in 30,300 h^{-1} GHSV at atmospheric pressure. NH_3 storage/TPD and several activity measurements were conducted in a temperature range of 150 to 500 °C for fresh and SO_2 poisoned catalyst. The SO_2 treatment was carried out twice by exposing the catalyst to 30 ppm SO_2 + 8% O_2 + 5% H_2O in Ar. After each sulfur treatment, the catalyst performance was evaluated for five times using standard SCR reactions until stable activity was reached (denoted SO_2-1A, SO_2-1B, SO_2-1C, SO_2-1D, SO_2-1E after first SO_2 treatment and SO_2-2A, etc after second sulfur treatment). This was followed by rapid SCR reaction, NO and NH_3 oxidation, NH_3 storage/TPD, and SCR reaction with 75% NO_2.

Results and Discussion

The SAPO-34 is a small pore zeolite and substantial amounts of either ion exchanged copper or other adsorbed molecules inside the zeolite cages are expected to decrease the micro-pore volume and such changes were observed upon SO_2 adsorption (Table 1). Note that the BET and V_p is based on estimated wash-coat amount. The monoliths contain a thin alumina layer and also binder, which lowers the BET surface area compared to pure Cu-SAPO-34..

Table 1. BET surface area and pore volume of the catalyst.

Monolith sample	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})
Cu-SAPO-34 fresh	431	0.27
Cu-SAPO-34 S-treated	318	0.21

The Cu-SAPO-34 catalysts exhibited high NO_x conversion activity and quite low NO and NH_3 oxidation activity. The activity in the redox reactions are mainly determined by the amount and the nature of the copper species in Cu-SAPO-34. Sulfur oxides are expected to have larger affinity to copper species compared with strong acid sites originating from the SAPO-34. Indeed the activity for NO_x reduction with NH_3 and NO significantly decreased upon catalyst exposure to SO_2 likely due to its adsorption on copper species (Figure 1). The concentration of adsorbed sulfur species can be significantly decreased upon exposure to high temperatures as seen from the recovery of NO_x conversion after repeated exposure to 500°C. Further, the catalyst exposure to sulfur oxides and its impact on various catalyst functions responsible for catalytic activity will be discussed.

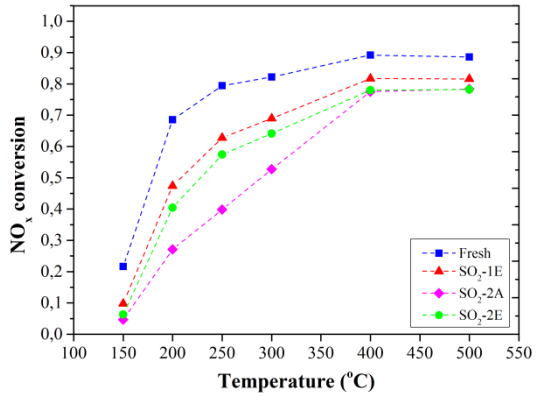

Figure 1. NO_x conversion during standard SCR over Cu-SAPO-34 after SO_2 treatment. The catalyst was exposed to 400 ppm NH_3, 400 ppm NO, 8% O_2, and 5% H_2O in Ar.

Significance

Ammonia SCR is one of the most important technologies for removing NO_x from diesel engine exhausts. Presence of sulfur oxides can degrade the SCR catalyst performance which can be restored by high temperature excursion. It is important to control such reversible degradation process for optimization of the working catalyst performance. In this work the impact of sulfur oxides on Cu-SAPO-34 catalyst functions were characterized and the knowledge is expected to improve catalyst performance management as well as can be used to develop kinetic models of deactivation.

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References

[1] Y. Cheng, C. Montreuil, G. Cavataio, C. Lambert, The Effects of SO_2 and SO_3 Poisoning on Cu/Zeolite SCR Catalysts, SAE International, (2009) 2009-01-0898.