A micro calorimeter study of ammonia adsorption over Cu Beta zeolite for urea SCR applications

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Introduction

The exhausts from diesel engines contain oxygen excess and the standard three-way catalyst cannot reduce the NO_x emissions during these conditions. One method is to use urea selective catalytic reduction (SCR). In this concept urea is fed to the exhaust gas stream and it decomposes to form ammonia. The ammonia reacts selectively with NO to produce N_2 and H_2O over a catalyst. Copper [1] and iron [2] exchanged zeolites as well as vanadia on titania [3] are possible catalysts. The composition of the exhausts changes very rapidly and it is therefore crucial to have a good insight into the kinetics of adsorption of ammonia on the catalyst. The objective with this study is to investigate the adsorption of NH_3 over Cu-Beta zeolites using a differential scanning calorimeter (DSC). This gives information about heat of adsorption, which can be used in kinetic modeling.

Materials and Methods

The catalyst powder was prepared by ion-exchange of a beta zeolite with a silica to alumina ratio of 38:1 from Zeolyst international. The powder was first ion-exchanged with $NaNO_3$ to get a more controlled ion-exchange and after that with a $(CH_3COO)_2Cu$ solution.

The heat during adsorption and desorption was detected using a differential scanning calorimeter (DSC), Sensys from Setaram. The reactor cell consists of a quartz tube with a sintered plate. The powder sample is placed on this plate. The gases are mixed using several mass flow controllers. Only a small fraction of the flow is used in order to get a more rapid switching when changing gas composition. The flow through both the reactor cell and the reference cell in the calorimeter was 10ml/min and the catalyst mass was 100mg.

Results and Discussion

We have investigated the adsorption and desorption of ammonia using micro calorimeter over Cu Beta zeolite at different conditions. Figure 1 shows the resulting thermogram from one experiment. The catalyst was first pre-treated for 20 min with 8% O_2 in Ar at 450 °C. This was followed by cooling the catalyst to 150°C in Ar and after that exposing the catalyst to 1000 ppm NH_3 for 80 min. When feeding the ammonia to the inlet gas feed stream, simultaneously a heat release of about 8 mW is observed in the calorimeter due to the adsorption heat. After about 37 min the heat signal goes back to zero again, because the catalyst is saturated with ammonia. When ammonia is turned off (t=160 min) there is a negative heat signal, due to the endothermic desorption of loosely bound ammonia. This is followed by a temperature ramp to 450°C while continuing exposing the catalyst to Ar only. During the ramp a broad negative peak is observed, due to desorption.

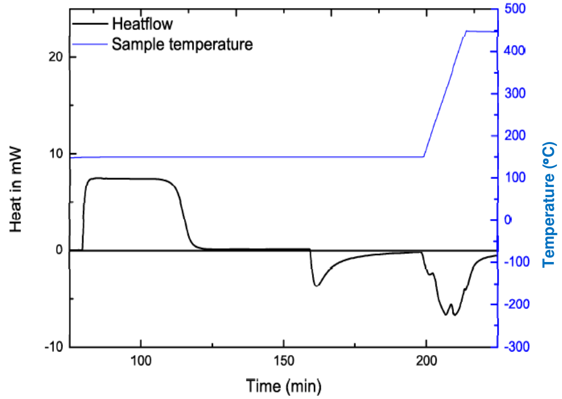

Figure 1. Thermogram from an experiment where exposing the Cu-Beta catalyst to 1000 ppm NH_3 for 80 min, followed by flushing the sample with Ar only and then heating the catalyst with a speed of 10 °C/min to 450°C. The sample size was 100 mg and the flow 10 ml/min.

Significance

Urea SCR is a very important technology for reducing NO_x from diesel and lean burn gasoline engines. Kinetic models are an important tool for predicting the emissions from the catalyst and also to gain a deep understanding of the mechanisms for the catalytic reactions. Since emissions from vehicles are strongly transient it is crucial to understand the adsorption of ammonia on different zeolite materials. The objective with this work is to measure the heat connected to ammonia adsorption over Cu-Beta and the results from this can be applied into kinetic models.

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References

1. Olsson, L., Sjövall H. and Blint, R.J. *Appl. Catal. B: Environmental*, 81 203 (2008).
2. Kröcher, O., Devadas, M., Elsener, M., Wokaun, A., Söger, N. Pfeifer, M., Demel, Y. Mussman, L., *Appl. Catal. B: Environmental* 66, 208 (2006).
3. Ciardelli, C., Nova, I., Tronconi, E., Chatterjee, D., Bandl-Konrad, B., Weibel, M. and Krutzsch, B., *Appl. Catal. B: Environmental*, 70, 80 (2007).