Urea-SCR activity of powdered catalyst at laboratory scale
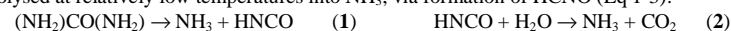
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Introduction

NOx reduction from Diesel and lean-burn engines is still a real challenge. Selective catalytic reduction (SCR) of NOx by ammonia (NH$_3$-SCR) is one of the effective NOx removal technologies. Unfortunately, direct use of ammonia is not suitable for vehicles and aqueous solution of urea, known as Adblue®, is commonly used as NH$_3$ precursor. Urea ((NH$_2$)$_2$CO) is hydrolysed at relatively low temperatures into NH$_3$, via formation of HCNO (Eq 1-3):

$$(NH_2)CO(NH_2) \rightarrow NH_3 + HNCO \quad (1) \qquad HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (2)$$

Overall reaction: $\quad (NH_2)CO(NH_2) + H_2O \rightarrow 2NH_3 + CO_2 \quad$ (3)

Ammonia can thereafter reacts with NOx, according to the well known NH$_3$-SCR reaction pathways (standard, fast and NO$_2$-SCR, depending to the NO to NOx ratio). Unfortunately, urea thermal decomposition can also lead to undesired by-compounds such as cyanuric acid, ammelide, biuret... Then, the conversion of urea to ammonia and/or the reactivity of by-products at the catalyst level have to be optimal. However, most of the laboratory catalytic benches use NH$_3$ as reductant, especially because urea injection is difficult to control and evaluations of the catalysts cannot take into account the "real" reaction mixture.

The aim of this work is to develop a urea-laboratory test in order to evaluate powdered catalyst in the urea-SCR catalytic reaction. In order to validate the experiments, the results are compared to well-controlled reaction of NH$_3$-SCR in standard condition.

Materials and Methods

The SCR catalyst was provided by Rhodia-Solvay. It is an acidic zirconia based oxide hydrothermally aged at 600°C (S$_{BET}$ = 50 m²/g). For catalytic tests, 100 mg of material was used, and the total flow rate was fixed at 20 L.h^{-1} (GHSV of about 160 000 h^{-1}).

The SCR activity measurements were carried out in a quartz tubular micro-reactor under 400-1000ppm NO, 10% O$_2$, 8-10% H$_2$O, 10% CO$_2$ balanced in N$_2$. Three types of tests were performed. For NH$_3$-SCR reference tests, 400 ppm NH$_3$ are added (NH$_3$-NOx ratio =1), and all gases were introduced using mass-flow controllers, except for H$_2$O (saturator). In order to develop injection of liquid reductant, tests with injection of an aqueous solution of NH$_3$ were primarily done (conditions 1 to 3, **Table 1**). The injection is performed into a heated zone (200°C) before the catalytic bed, using a micro-nozzle provided by The Lee Compagny. The liquid flow rate is controlled by a micro HPLC pump (Jasco). Finally, for urea-SCR experiments, an aqueous solution of urea (0.8wt%) was used (condition 4). All gases were analyzed by FTIR (MKS 2020) and the catalytic reactor was initially maintained at 300°C.

Results and Discussion

Figure 1A reports the NH$_3$ and H$_2$O profiles corresponding to conditions 1 to 4. For conditions 1 – 3, the expected amount in regards of experimental setups (**Table 1**) is about 1000 ppm NH$_3$ and 10% H$_2$O. For condition 4, the theoretical amount is 800 ppm NH$_3$ considering a total urea decomposition, and 8% H$_2$O. From **Figure 1A**, it appears that the aperture diameter of the micro-nozzle is a key parameter for the stability of the resulting compounds vapour. In fact, both a very good correlation and high stability is obtained with the

condition 4 setup, which was kept for further urea-SCR catalytic tests. Thereafter, the influence of residence time (between the urea injection and the catalytic bed) on the DeNOx efficiency was studied and compared to the results of the NH$_3$-SCR light-off test (200-500°C). Results were depicted in **Figure 1B**. Very similar profiles were obtained in NH$_3$-SCR and urea-SCR when test with urea was performed with the shorter residence time (5.2s, green curve). It is advanced that, reducing the residence time improves the secondary emissions of ammonia from the reducing agent (Eq. 2), as previously reported in [1].

Table 1. Experimental conditions of catalytic tests.

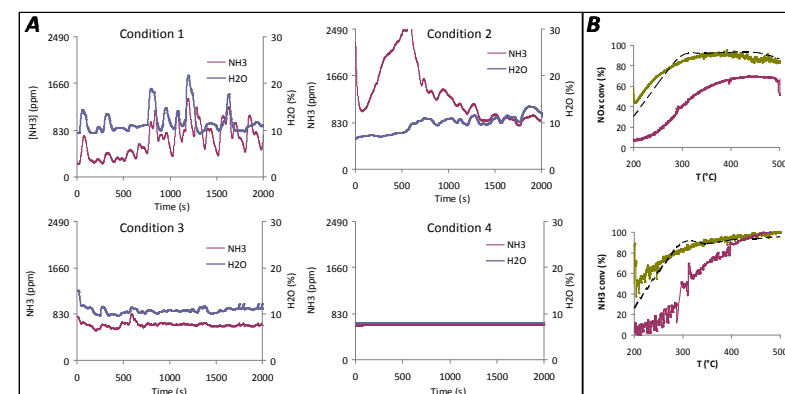|	Condition 1	Condition 2	Condition 3	Condition 4
Ø$_{nozzle}$ (µm)	200	170	100	50
ΔP HPLC pump (Bars)	5–6	5–6	7–8	9–10
D$_{aqeous sol.}$ (µL.min^{-1})	24 (NH$_{3 aq}$)	24 (NH$_{3 aq}$)	24 (NH$_{3 aq}$)	20 (urea $_{aq}$)

Figure 1. A: NH$_3$ and H$_2$O profiles versus time on stream without catalyst, T(injection) = 200°C, T(catalytic reactor) = 300°C. B: Influence of urea residence time in urea-SCR. (━: 5.2s ; ━: 6.3s ; ---: NH$_3$-SCR). Gas: 800ppm NO, 10% O$_2$, 10%CO$_2$, N$_2$ balanced.

Significance

This work demonstrates the feasibility of an urea-SCR catalytic test at micro-laboratory scale using powder catalysts, which is poorly developed in the literature. Steady-state kinetic experiments, to determine reaction order with respect to NOx and "NH$_3$" and apparent activation energies, for urea-SCR compare to NH$_3$-SCR is thereafter considered.

Acknowledgements

Reference

[1] M. Koebel, M. Elsener, M. Kleemann, Catal. Today 59 (2000) 335-345.