ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Novel method of ammonium nitrate quantification in SCR catalysts

Maria Pia Ruggeri[a], Jinyong Luo[b], Isabella Nova[a], Enrico Tronconi[a,*], Krishna Kamasamudram[b], Aleksey Yezerets[b]

[a] *Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy*
[b] *Corporate Research & Technology, Cummins Inc., Columbus, IN, USA*

ARTICLE INFO

Keywords:
NH_3-SCR
NH_4NO_3
N_2O
N balance
Zeolites

ABSTRACT

NH_4NO_3 or Ammonium nitrate (AN) can be formed onto NH_3-SCR catalysts in the low-T range typical of urban or low-load operation, resulting in self-inhibition of the catalysts. Also, subsequent decomposition of AN during high-temperature transients may lead to the undesired formation of N_2O, a potent greenhouse gas. Quantification of AN formation and decomposition has been not adequately addressed so far due to experimental difficulties.

We propose an original method for measuring the amount of AN formed on SCR catalysts, and validate it in bench-flow runs over a commercial Cu-CHA formulation. In order to quantify the AN on the catalyst, we rely on its reaction with NO according to $NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O$, further investigated via DRIFTs in this work. Based on this stoichiometry, the amount of deposited AN can be estimated from the integral molecular balances of reliably and precisely measurable species, such as NO and NO_2. This approach is initially applied over catalyst powder in a rig where N-balances could be evaluated directly, and subsequently validated over more realistic coated monolith catalyst samples in a bench-flow reactor in which N_2 was used as carrier gas. In the validation tests, known amounts of AN were initially deposited on the catalyst by controlled pre-dosing of an AN aqueous solution: such amounts were found in satisfactory agreement with the estimates obtained by our method. We expect the proposed methodology for AN quantification to be generally applicable to other types of SCR catalysts as well, including V-based systems and Fe-zeolites.

1. Introduction

Selective Catalytic Reduction of nitrogen oxides with NH_3 derived from urea solution (NH_3-SCR) is the leading technology for meeting the increasingly stringent environmental regulations applied worldwide [1]. Among many variants of SCR catalysts, metal-exchanged zeolites and, in particular, Cu-zeolites with a CHA structure have gained particular popularity, due to their desirable performance and especially due to their unmatched hydrothermal stability [2]. While broadly recognized for their outstanding activity already at temperatures as low as 200 °C, these catalysts may not behave as well at lower temperatures, which, however, can be encountered in typical urban or low-load operation. Indeed, although urea could be injected in the aftertreatment systems already at $T > 180$ °C, Cu-zeolites may exhibit poor activity in this temperature region. In fact, due to the excess of NO_2 produced over the upstream DOC device already when the SCR catalyst is below 200 °C, the following reaction may occur (R.1).

$$2NH_3(ads) + 2NO_2(g) \rightarrow NH_4NO_3(s) + N_2(g) + H_2O(g) \qquad (R.1)$$

resulting in the undesired formation of ammonium nitrate (AN) salt [3,4]. The phenomenon described by R.1 produces very slow transients in which the solid reaction product AN is deposited onto the catalyst surface: because of AN build up, the catalyst activity is slowly and progressively inhibited during sustained operation at low temperatures.

Notably, at temperatures above approximately 170 °C AN sublimation occurs according to (R.2) [5]:

$$NH_4NO_3(s) \leftrightarrow NH_3(g) + HNO_3(g) \qquad (R.2)$$

NH_3 and HNO_3 thus leave the reactor in the gas phase, but they may re-condense in a cold spot downstream, leading to the formation of solid deposits, eventually building up flow resistance and possibly leading to clogging of the exhaust lines in laboratory equipment [3,4].

At slightly higher temperatures, e.g. during heat-up transients, part of the AN deposited on the catalyst can thermally decompose to undesired N_2O [3,4], a well-known greenhouse gas, according to (R.3):

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g) \qquad (R.3)$$

Despite high probability of occurring under normal operating

---

[*] Corresponding author.
E-mail address: enrico.tronconi@polimi.it (E. Tronconi).

http://dx.doi.org/10.1016/j.cattod.2017.04.016
Received 30 September 2016; Received in revised form 10 March 2017; Accepted 7 April 2017

Please cite this article as: Ruggeri, M.P., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.04.016

conditions of aftertreatment systems, the AN self-inhibiting effect remains relatively poorly investigated and modeled, because its description is complicated by the empirical measurement uncertainties of AN formation. Indeed, quantification of AN is not trivial: first of all, sublimation/vaporization of the in-situ produced AN may potentially occur, according to (R.2); furthermore, an accurate quantification of AN deposited on the catalyst through (R.1) would require measurements of N_2 along with other N-containing species, as a means of closing the N atomic balance. This presents an insurmountable challenge when testing catalysts in gas feeds closely simulating diesel exhausts, which contain large amounts of N_2.

On the other hand, under SCR reacting conditions, AN can be transformed into species that can be reliably and precisely measured, which might provide potential opportunities for its quantification. For example, AN is reported to react readily with NO over SCR catalysts to form gaseous NO_2 [3,4,6–8]:

$$NH_4NO_3(s) + NO(g) \rightarrow N_2(g) + NO_2(g) + 2H_2O(g) \tag{R.4}$$

This reaction is also reported [9,10] as a route to enhance the deNOx efficiency over V-based and Fe-exchanged zeolite catalysts at 200–300 °C: the strategy consists in dosing suitable amounts of aqueous solution of AN into the exhausts which, by reacting with NO, will form NO_2. NO_2 can then react with additional NO according to the Fast SCR reaction:

$$2NH_3(ads) + NO(g) + NO_2(g) \rightarrow 2N_2(g) + 3H_2O(g) \tag{R.5}$$

characterized by rates significantly higher than the Standard SCR reaction, wherein NO only reacts with NH_3.

In this work, we propose a method for the quantification of AN deposited on SCR catalysts based on its reactivity with NO, (R.4). The method was first developed designing dedicated experiments which required the use of a mass spectrometer and He as carrier gas in order to quantify N_2 production along with NO_2 and NO consumptions. In these experiments, AN was produced in situ by direct reaction of NO_2 and NH_3 on a commercial Cu-CHA catalyst powder, and then completely reacted with NO. An integral N-balance was performed, which enabled a comparison of the AN deposited onto the catalyst in the first part of the run, with the amount of AN estimated by its reaction with NO in the second part of the run. In a subsequent stage, the method was validated on small core monoliths of the same catalyst, tested under more realistic conditions in terms of GHSV and gas feed composition (N_2 as carrier gas). In these validation runs, a known amount of AN was dosed to the catalyst in the form of an AN solution and successfully compared to the amount estimated by NO titration, without the need for a direct measurement of N_2.

We believe that the same formalism and methodology herein presented for AN quantification could be applicable to other types of SCR catalysts as well, based on the commonality of the underlying chemistry and stoichiometric relationships described in this work.

2. Experimental/methodology

A commercial Cu-Zeolite formulation of the CHA type has been used throughout this study.

2.1. Preliminary catalytic activity study

For NH_3-SCR catalytic activity measurements, a cylindrical catalyst core of 2.54 cm diameter and 7.62 cm length was used in a bench-flow reactor system. Simulated exhaust gases (200 ppm NOx, 200 ppm NH_3, 10% O_2, 8% CO_2, 7% H_2O, balance N_2 v/v) containing different NO_2/NO_x molar feed ratios (from 0 to 0.8) were fed to the catalyst at a total flow rate of ~26 slpm, corresponding to a gas hourly space velocity (GHSV) of approximately 40,000 h^{-1}. The feed and effluent gas compositions were analysed by an MKS MultiGas 2030 FTIR. Before testing, the sample was pretreated at 550 °C for 4 h in the base feed gas (10% O_2, 8% CO_2, 7% H_2O, balance N_2 v/v).

Gas phase analysis of the products was accompanied by *in situ* DRIFTS measurements to investigate the formation of surface species and their reactivity with NO. For this purpose, Cu-Zeolite powder samples scraped from the cores were loaded in a DRIFTS reactor cell (Nicolet 6700 spectrometer equipped with Praying Mantis high-temperature DRIFTS cell, Harrick temperature control box and gas manifold assembled in house), pre-treated at 500 °C in 10% O_2/Ar for 30 min and subsequently cooled to 150 °C. Then, background spectra were collected after the gas switched to 2% H_2O at 150 °C for 30 min. After that, NH_3 (200 ppm NH_3/Ar) was introduced to the sample for 3 h, followed by NO_2 (200 ppm), or NO_2 + NH_3 (200 ppm NO_2, 200 ppm NH_3, balance Ar) for AN deposition. Last, NO (200 ppm NO/Ar) was introduced to react with the AN deposited on the surface for 1 h. All the adsorption and reaction tests were performed at 150 °C, in the presence of 2% H_2O. The DRIFTS spectra were recorded in the range of 4000–650 cm^{-1} at 64 scans with a resolution of 4 cm^{-1}.

2.2. Tests for AN estimation

2.2.1. Powder testing

The method for the quantification of AN deposition was developed using a micro-reactor rig: 80 mg of the commercial Cu-CHA catalyst were crushed, sieved to 90 μm average particle size, diluted with cordierite and then loaded in a quartz tubular microreactor. The reactor was then inserted in a furnace and the temperature of the experiment, typically 180 °C, was controlled by a thermocouple immersed in the catalyst bed. All the lines downstream from the reactor were heated at T = 200 °C to prevent AN deposition in cold spots, which could affect the analysis and quantification of the reaction products during the experiment.

The rig was equipped with a mass spectrometer and a UV analyser for the simultaneous measurement of all the N-containing gases: N_2, N_2O, NH_3, NO and NO_2. Calibrated mass flow controllers allowed feeding of the desired gas mixture for the in-situ generation of AN: typically, 500 ppm of NO_2 and NH_3 were fed in a total flow of 120 Ncc/min. Prior to each experiment, the catalyst was exposed to 8% O_2 in He at 550 °C for 1 h. All the gases were fed from cylinders containing a synthetic mixture of the desired gases and Ar (used as tracer for mass quantification); He was used as carrier gas in order to enable N-balance estimation. Additional experimental details have been described elsewhere [4].

2.2.2. Monolith testing

The method developed for AN quantification on the powdered catalyst was validated using a small core monolith (V = 6 cm^3) coated with the same Cu zeolite material. The sample was loaded and tested in a stainless steel reactor tube inserted in a furnace . The temperature of the experiment, typically 180–200 °C, was monitored by a thermocouple inserted into the central channel of the monolith. In these experiments the carrier gas was N_2, and a 0.1 M AN solution was fed to the catalyst at a known rate using a peristaltic pump [10]. The gas stream leaving the test reactor was monitored by a UV analyser for NO, NO_2 and NH_3 detection, and by an IR analyser for N_2O measurement.

All the validation experiments have been carried out at a constant GHSV of 25000 h^{-1}, feeding different concentrations of AN (100, 150, 200 ppm) by changing the operative conditions of the peristaltic pump. The overall amount of AN loaded on the catalyst was controlled by changing the AN solution feed time, Δt, according to:

$$AN_{fed} = \frac{ppmAN \times Q \times \Delta t}{22.41 \times 10^6}[moles] \tag{1}$$