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Sensor and method for determining the ammonia loading of a zeolite SCR catalyst

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Abstract

A sensor and a method for determining the NH_3 loading of a base-metal zeolite catalyst are described. This catalyst material is used to reduce NO*x* emissions in diesel exhaust via reaction with injected NH_3, a process known as selective catalytic reduction (SCR). Some of the injected NH_3 is stored on the catalyst surface before it reduces NO*x*. We demonstrate that the catalyst material itself can be used as part of a sensor measuring the level of stored NH_3. The AC conductivity of a thick film of the catalyst material was measured at 4 Hz and was found to increase when NH_3 was introduced into the gas phase, eventually saturating presumably as the material reached its maximum NH_3 storage capacity. The conductivity was monitored as the temperature was raised sufficiently to desorb (or oxidize) most of the stored NH_3. The resulting change in the conductivity upon heating was used as a measure of the NH_3 loading level on the zeolite catalyst material. We demonstrate this parameter is dependent on NH_3 concentration, NH_3 loading time and gas temperature.

Keywords: Ammonia sensing; Zeolite; SCR catalyst; Desorption

1. Introduction

The reduction of nitrogen oxide (NO*x*) emissions from diesel vehicles is made difficult due to the elevated O_2 levels present in diesel exhaust. However, the urea/SCR (SCR = selective catalytic reduction) exhaust after-treatment system has been shown to be effective in reducing the NO*x* emissions, with low impact on fuel economy [1]. In this system NH_3, formed from the injection of aqueous urea, reacts selectively with NO*x* on the SCR catalyst to form N_2 and H_2O. The SCR catalyst can be a base-metal zeolite material typically operating most efficiently above 200 °C, and has the ability to store some of the injected NH_3 [2]. The NH_3 storage capacity for common SCR catalyst materials, however, is reduced with elevated temperature [2,3]. For optimal performance, the levels of NH_3 injected into the exhaust must match the NO*x* emissions over a specific time interval. Under-injection of NH_3 leads to a lower NO*x* conversion rate and the inability to meet the regulated emission standards. Over-injection gives yields unreacted NH_3, which is an undesirable emission. A catalyst fully saturated with stored NH_3 has the positive benefit of yielding a high NO*x* conversion rate. However, the maximum amount NH_3 stored on the SCR catalyst decreases with temperature. Thus, a catalyst saturated with NH_3 would liberate some of it upon excursions to high-exhaust gas temperatures, resulting for that case unwanted exhaust emission.

The goal of the SCR catalyst system is to minimize both NO*x* and NH_3 emissions by the proper control of the aqueous urea injection. In principle this can be achieved via control of the stored NH_3 levels along the axial length of the catalyst, with high-NH_3 loading in the upstream portion of the catalyst to ensure high NO*x* conversion and lower NH_3 loading in the downstream portion to minimize NH_3 emissions. One method to maintain an optimal NH_3-loading profile along the SCR catalyst is based on accurate models of parameters such as the NO*x* levels emitted by the engine, quantity of urea injection, temperature, gas flow, NO*x*–NH_3 reaction rates and NH_3 storage. This approach can be improved using NO*x* and/or NH_3 sensors located downstream of the catalyst, providing feedback to help ensure that the slip of these gases are minimized. We demonstrate here a further possible improvement: By locally heating and desorbing the NH_3 stored on a portion(s) of the SCR catalyst while simultaneously monitoring its ionic conductivity, it is possible to obtain an estimate of the quantity of stored-NH_3 in that region. We demonstrate a sensor concept based on this temperature-programmed-desorption related technique.

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Moos et al. reported that zeolites such as H-ZSM5 to be a surface proton conductor whose ionic conductivity is enhanced in the presence of NH_3, enabling them to be used as the basis of a selective NH_3 sensor [4]. The fundamental sensing principle is that the mobility of H^+ along the surface is enhanced by their reaction with NH_3 to form $NH_4{}^+$ ions, which are bound less tightly and have lower activation energy for hopping along the zeolite surface [5]. In a similar fashion, we show here that the base-metal zeolite material used in the SCR catalyst can also be used to detect NH_3. We suggest that the amount of NH_3 stored on the catalyst material can be estimated by monitoring its change in conductivity upon heating to temperatures sufficient to desorb or oxidize most of the stored NH_3. We demonstrate that by sacrificing continuous measurement of the NH_3-storage levels and measuring instead that thermally desorbed upon rapid heating, we obtain greater signal. Occasional measurements of the NH_3 storage levels are expected to be sufficient to update the previously described urea-injection control models.

2. Experimental

The basic sensor configuration is shown in Fig. 1. The main component is a base-metal zeolite catalyst material (proprietary composition) that was deposited as a thick film on an alumina substrate. Contained within the alumina substrate is an embedded heater, enabling the temperature of the catalyst film to be raised to 600 °C. The heated area is ~5 mm by ~5 mm. The catalyst film was also laid over a pair of metal electrodes, which were used to monitor its conductivity. The electrodes are configured as two parallel strips with ~0.5 mm separation and which covered the entire heated region. The zeolite film was made by spreading a slurry containing a powder of the base-metal zeolite catalyst material mixed with a colloidal alumina solution (~50 nm alumina particle size). The slurry was dried to a thick film using heated air. The alumina was added as a binder phase and was ~20% of the final film by weight. Exact film thickness was not determined.

In our tests, the conductivity was measured by monitoring the current induced upon applying a 5 $V_{P–P}$ sinusoidal signal at 4 Hz. The root mean square (rms) magnitude of the resulting current was measured using a Stanford Research Systems Model SR850 DSP lock-in amplifier. All data were taken in background gases of 5% O_2 and 1% water, with the balance N_2, using a laboratory gas flow bench.

Since we are describing monitoring the conductivity changes in the thick-film zeolite upon thermally desorbing the stored NH_3, we define two operational modes: the NH_3 loading mode and the measurement mode. Prior to the start of the NH_3 loading mode, the sensor was free of stored NH_3. During the loading mode the temperature was held constant while a fixed concentration of gas-phase NH_3 was exposed to the sensor, some of which was stored on the catalyst material. Constant temperature during loading mode, T_L, was achieved by placing the sensor in quartz tube that was inserted into a tube furnace. In our experiments power was not applied to the sensor's substrate heater during this mode. However, during the measurement mode a 9 V signal was applied to the substrate heater causing the temperature to rise sufficiently above T_L to desorb or oxidize most of the NH_3 that was stored during the loading mode. The amount of NH_3 stored during the loading mode was determined from the change in the catalyst conductivity as the temperature was increased. We monitored this change in conductivity upon heating, testing for the influences of NH_3 loading time, NH_3 loading temperature, and NH_3 concentration.

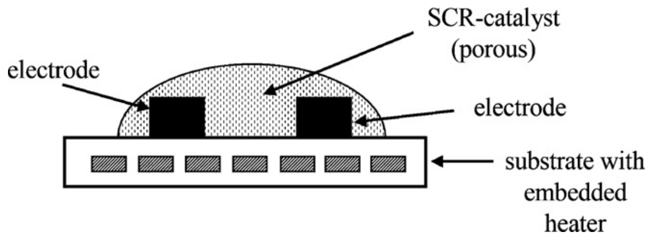

Fig. 1. Cross-section of the SCR catalyst conductivity sensor.

3. Results

Fig. 2 shows the rms current measured across the thick-film sensor as a function of time for both the NH_3 loading mode and the subsequent measurement mode. For both of these time intervals the film was exposed to 400 ppm NH_3, which was introduced at $t = 0$. Prior to this time the sensor was free of stored NH_3. The first 40 min of Fig. 2 describe the loading mode, during which the temperature was held at ~267 °C. Note that during this time period the conductivity of the zeolite catalyst film slowly increased, approaching an asymptotic value after ~30 min. The measurement mode was initiated at $t = 40$ min for the data shown in this figure. At that time 9 V was applied to the substrate heater. It is presumed that the rapid rise and subsequent decrease in the measured current during that time interval was a result of the rapid increase in the sensor temperature to values sufficient to

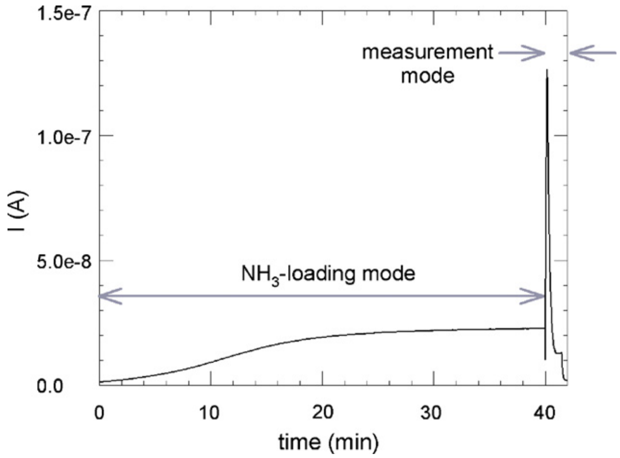

Fig. 2. The AC current as a function of time for the thick-film zeolite sensor. The composition of the background gas was 5% O_2 and ~1% water in N_2. Prior to $t = 0$, the sensor was free of stored NH_3. At $t = 0$, 400 ppm NH_3 was introduced and kept on during the test. The sensor temperature was ~267 °C for the first 40 min. This time interval is labeled NH_3 loading mode. After $t = 40$ min, the temperature of the sensor was raised sufficiently to desorb/oxidize most of the stored NH_3. This time interval is labeled measurement mode.