(EtOH+NH_3) synergism in lean-NOx reduction over Ag/Al_2O_3 catalyst

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Abstract: The implemented Urea-SCR technology is an effective process for NO_x reduction from Diesel vehicles but is strongly dependent at low temperature (175-250°C) to the NO_2/NO_x ratio. By means of co-feeding of ammonia and ethanol over Ag/Al_2O_3 catalyst, a drastic enhancement of the NO_x conversion is evidenced using only NO as NO_x. The ammonia activation is mainly attributed to the availability of hydrogen H* species resulting from EtOH oxidation. A remarkable $DeNO_x$ efficiency is additionally achieved with a dual-bed configuration (Ag/Al_2O_3+NH_3-SCR catalyst) leading to impressive performances of this EtOH-assisted process without critical dependence to the NO_2 yield.

Keywords: SCR, $DeNO_x$, Ag/Al_2O_3.

1. Introduction

Reduction of NO_x compounds from Diesel and lean burn engine remains a major challenge at low temperature. The selective catalytic reduction (SCR) of NO_x by urea/NH_3 is well established and used worldwide to convert NO_x into nitrogen, according to the so-called standard-SCR reaction (Eq. 1)[1]:

$$2NH_3 + 2NO + ½O_2 \rightarrow 2N_2 + 3H_2O \qquad \text{(Eq. 1)}$$

However, in this condition, the activity at low temperatures (175-250°C) remains limited and improvement requires prior oxidation of NO to NO_2 to promote the more favorable fast-SCR reaction (Eq. 2):

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad \text{(Eq. 2)}$$

NO_2 yield can be adjusted by the Diesel oxidation catalyst (DOC) upstream the SCR converter. In practice, the NO_2/NOx ratio depends on the DOC activity, which also undergoes kinetic limitation at low temperature and penalizes the $deNO_x$ efficiency of the SCR converter downstream.

EtOH-SCR process was also described as an attractive way to reduce NO_x with silver-based catalyts[2]. The NO conversion is assumed to be strongly dependent of the nitromethane route formation, based on the ethanol oxidation to acetaldehyde *via* a variety of intermediates which are subsequently adsorbed as surface acetate and ethoxide ions. N-containing compounds such as HNCO and ammonia are also involved in the NO_x reduction mechanism[3]. Unfortunately, this system also suffers from limited activity at low temperature, although partial oxidation of ethanol leads to high NO_2 emission in the 175-300°C temperature range[4].

This work aims to demonstrate the beneficial co-feeding of ethanol and ammonia (EtOH/NH_3-SCR) over Ag/Al_2O_3 to enhance the low temperature NO_x reduction in the unfavorable standard-SCR condition.

2. Experimental

2%Ag/Al_2O_3 (Ag/Al) and $WO_3/Ce_xZr_{1-x}O_2$ (WO_3/Ce-Zr) catalysts were prepared according to ref 5. Catalytic tests were performed in a quartz tubular micro-reactor under a synthetic flow containing or not 1200ppm EtOH, with or without 400ppm NH_3, 400ppm NO, 8% H_2O, 10% CO_2, 10% O_2, N_2. Three reductants were evaluated, namely ethanol (EtOH), NH_3, and a blend (EtOH+NH_3). Gaseous $NO/NO_2/NH_3/O_2/N_2$ gas flows were adjusted by mass-flow controllers (Bronkhorst). Ethanol aqueous solution ($8.02\ 10^{-1}$ mol L^{-1}) was vaporized and mixed upstream the SCR catalyst by means of a micro-nozzles provided by The Lee Company ($Ø_{nozzle}$= 50 µm) connected to a HPLC pump (Jasco, PU-2085, 22 µL min^{-1}, ΔP=10 Bar). The compositions of the feed gas and effluent stream were monitored continuously using online MKS 2030 Multigas infrared analyser for NO, NO_2, N_2O, HNCO, NH_3, CH_3CH_2OH, CH_3CHO, CH_3OH, CH_2O, C_2H_4, CH_4, CO, CO_2 and H_2O.

3. Results and discussion

The effect of reducers (NH_3, EtOH and EtOH/NH_3) on NO_x conversion over Ag/Al catalyst (full line) is reported in Figure 1A. With ethanol as reductant (EtOH-SCR), NO_x conversion was 9% and 38% at 200 and 250°C, respectively (blue curve). When ammonia was co-feeded in the mixture, an important gain was denoted (green curve). The NO_x conversion reached 33% and 74% at 200°C and 250°C, respectively. No significant NO_x conversion was recorded with only ammonia whatever the temperature (yellow curve), which means that the ammonia activation is due to the presence of ethanol over Ag/Al sample.

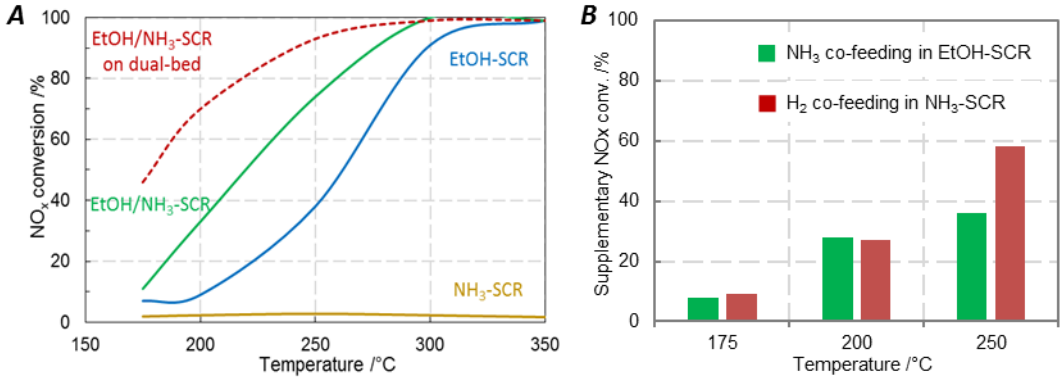

Figure 1. (A): Effect of the reducers used on the NO_x conversion profile over Ag/Al (full line) or a dual-bed system Ag/Al+WO_3/Ce-Zr (dotted line); (B): Comparison of H_2 addition in NH_3-SCR and NH_3 addition in EtOH-SCR over Ag/Al.

As reported in Figure 1B, this EtOH+NH_3 synergistic effect is mainly attributed to the ethanol dehydrogenation leading to the formation of surface hydrogen H^* ad-species allowing a mechanism related to H_2 assisted NH_3-SCR process over Ag/Al catalysts[6]. Our hypothesis, supported by the characterization of adsorbed species followed by FTIR, is that these H^* species are involved in HNO_x species, which are known to be very reactive with NH_3[7].

However, in this EtOH/NH_3-SCR process over Ag/Al, unconverted NH_3 and NO_x remained. To further improve the NO_x conversion, experiments were carried out adding a conventional tungsten based NH_3-SCR catalyst downstream to Ag/Al sample. In this dual-bed system, the NO_x conversion profile (Figure 1, red dotted line) exhibited a supplementary significant improvement. The NO_x conversion varied from 46 to 95% in the 175-250°C temperature range. This high activity is due to a supplementary conversion occurring on the NH_3-SCR catalyst, via the fast-SCR reaction.

4. Conclusions

The NH_3-EtOH-SCR process over Ag/Al catalyst was evidenced to significantly improve the NO_x reduction at low temperature in the unfavorable standard SCR condition. The formation of H^* species (from ethanol oxidation) is proposed to promotes the NH_3-SCR over Ag/Al_2O_3. Moreover, NO_2 (from NO+EtOH reaction) can be used in a dual-bed coupled system composed of Ag/Al and a conventional NH_3-SCR catalyst to supplementary improve the NO_x reduction by NH_3. A remarkable enhancement of the deNOx efficiency was achieved without dependence to the activity of the upstream oxidation catalyst (DOC). It makes this process an attractive way to increase the crucial low temperature SCR activity in NO-rich media and offer promising new avenue to achieve the future stringent regulations of lean-burn passenger cars.

References

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