Advantages of Syngas for the Regeneration of NOx Trap System Investigated with Operando IR Measurements

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Introduction and Objectives

Lean NO_x trap/reduction systems (NSR) for Diesel fuelled engines currently run in sequential conditions with lean and short rich period that ensure the reduction of stored NO_x to N_2. Subsequent improvement can be achieved by injecting upstream the NSR system a reformate composed of CO + H_2. In the presence of H_2, less attention was paid to the formation of side products during the regeneration process. The production of NH_3 as side product for example can be profitably used to improve the efficiency by coupling the NSR catalyst with a Selective Catalytic Reduction system. Operando in situ infrared spectroscopic investigation was thus performed for the examination of adsorbed species and the simultaneous analysis of N_2, N_2O and NH_3 products particularly for high H_2 and CO concentrations. A specific attention was paid to the influence of time and to the composition of the regeneration between 150 and 350°C.

Materials and Methods

The catalyst (1%wt Pt-0.5%wt Rh/Al_2O_3-BaO) is grinded and pressed into a self-supported wafer (11.6mg) before being placed in the IR reactor in transmission mode as previously described[1]. Storage is achieved in the presence of 500ppm NO+5%O_2 during 120s-500s whereas regeneration is performed using 2-20%H_2+0-5%CO+He during 1-60s. The switches lean/rich are repeated 20 times with a 4-ways valve for each condition in order to stabilize the activity. The formation of N_2, N_2O and NH_3 is followed using IR spectroscopy (380 Thermo) and mass spectrometry (Pfeiffer). The nature of adsorbed species is recorded on an FTIR 460 Protégé (Thermo) spectrometer fitted with MCT detector and using 64 scans per spectra at 4 cm^{-1} (1spectra/13 s).

Results and Discussion

The regeneration of NOx trap catalyst (Pt-Rh/Al_2O_3-BaO) with high H_2 concentration showed the involvement of nitrite and nitrate in function of temperature and regeneration time. Bridging nitrites were accumulated at 150°C (Fig. 1) and were transformed during long time regeneration (60s) mainly into NH_3. Nitrite and nitrate developed at 250°C. Two processes leading to the formation of products occurred during lean/rich and rich/lean switches, inducing a change in selectivity. In the presence of 5%CO (no H_2), an extensive production of N_2O was observed at 250°C. The addition of H_2 to CO was accompanied by an attenuation of N_2O formation and significant

production of NH_3. Spectra of the adsorbed species which accumulate were recorded during the regeneration phase with two different relative concentrations of H_2 and CO (Fig. 2). No signal appears at the end of storage phase in the spectral range 1800-2400 cm^{-1}. After CO/H_2 injection, the carbonyl species over noble metals as well as NCO over alumina [2] developed at 2040, 2080 cm^{-1} and at 2250 and 2230 cm^{-1} respectively.

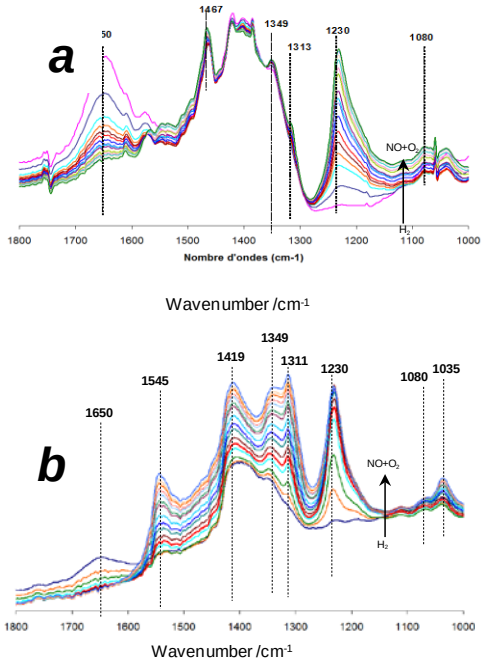

Figure 1. Infrared spectra recorded during the storage phase with 6%H_2 at 150°C (***a***) and 250°C (***b***) (storage 500s, regeneration 60s)

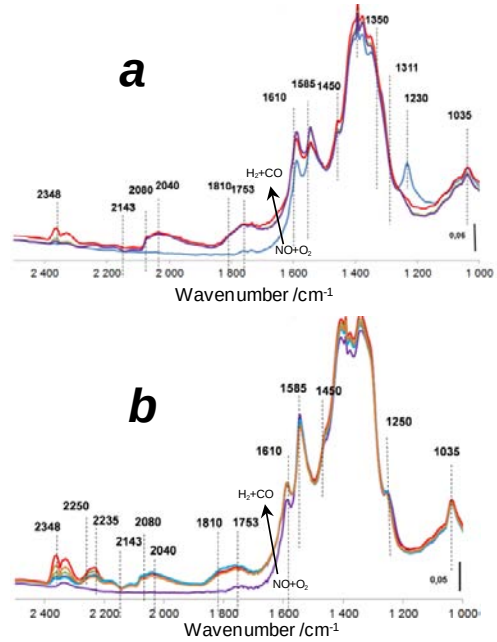

Figure 2. Infrared spectra recorded during the regeneration phase with 1%CO+4%H_2 (***a***) and 4%CO+1%H_2 (***b***) at 250°C (Storage 120s, regeneration 60s)

In presence of CO the formation of nitrite and its regeneration was progressively inhibited. This could explain the decrease of NOx trap efficiency at low temperature. The beneficial effect of H_2 addition at 250°C which promotes the formation of NH_3 could arise from hydrogenolysis of NCO species as well as usual successive hydrogenation of chemisorbed N atoms from NO dissociation.

Conclusions

Owing to high H_2/CO content in syngas, strong differences in the distribution of adsorbates in function of the relative CO/H_2 composition were observed. The changes of selectivity into N_2, N_2O and NH_3 were related to the operating conditions and the nature of adsorbates. The influence of regeneration time gave further information for further coupling of NOx trap catalyst with Selective Catalytic Reduction catalyst. The latter could promote the NOx SCR with ammonia produced from NOx trap catalyst.

References

1. T. Lesage et al., Topics Catal. 30–31 (2004) 31
2. N. Bion et al., J. Catal. 217 (2003) 47–58