Transient isotopic study of low-temperature NO_x reduction by H_2 on $Pt/Mo/ZrO_2$ catalyst

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Significance and Relevance

Steady State Isotopic Transient Kinetic Analysis (SSITKA) and in-situ diffuse reflectance infrared spectroscopy (DRIFTS) was used to study the mechanism of low-temperature NO_x reduction by H_2 in lean exhaust gas using highly active $Pt/Mo/ZrO_2$ catalyst [1]. SSITKA clearly shows the participation of adsorbates at the interface around the Pt particles. Moreover, in-situ DRIFTS experiments with isotopic switch from H_2 to D_2 elucidates an additional reaction path toward the formation of N_2 involving NH_x species coordinated to strong acid sites of highly dispersed MoO_x moieties.

Preferred and 2nd choice for the topic:
Fundamental advances in understanding catalysis, Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

For NO_x removal from lean automotive exhaust gases, selective catalytic reduction (SCR) and NO_x storage catalysts are established technologies, whereas they operate efficiently only above 175°C. Contrary, future NO_x emissions limits (e.g. Euro-7) will require an effective abatement of NO_x even at low temperatures. For this purpose, the NO_x reduction by H_2 (H_2-deNO_x) on Pt catalysts is a promising technique. However, these catalysts still suffer from significant N_2O and/or NH_3 by-production. Recently, the modification of Pt/ZrO_2 with Mo [1] and W [2] was reported to provide both high activity at low temperatures as well as reduced N_2O and NH_3 emissions. Moreover, enhanced strong Lewis acidity of $Pt/Mo/ZrO_2$ was found to improve N_2 formation, suggesting a highly selective additional SCR-related mechanistic deNO_x pathway [1]. Therefore, this study aims to unravel the reaction mechanism of NO_x reduction by H_2 on $Pt/Mo/ZrO_2$ combining SSITKA and in-situ DRIFTS studies.

Materials and Methods

$Pt/xMo/ZrO_2$ catalysts were prepared by incipient wetness impregnation of monoclinic ZrO_2 with $Pt(NO_3)_2$ (w(Pt) = 0.25 wt.%) and $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ (w(Mo) = 0 and 3 wt.%) with subsequent 5h calcination at 500°C. SSITKA experiments were used for in-situ quantification of reactive species in H_2-deNO_x reaction. After rapid switching from ^{14}NO to ^{15}NO by a pneumatic 4-way valve, the evolution of the isotope-labelled products was monitored using an online mass spectrometer. Kr served as inert tracer to correct the gas phase hold-up. Furthermore, in-situ DRIFT spectroscopy enables the identification of adsorbates at the surface of working catalyst. The red shift of the IR bands following the switch from ^{14}NO to ^{15}NO and H_2 to D_2 was used to discriminate reactive from inactive species. All measurements are performed in lean synthetic exhaust gas (200 ppm $^{14}NO/^{15}NO$, 5% O_2, 2000 ppm H_2/D_2, Ar balance, GHSV = 70.000h^{-1}) after reaching steady state at 90°C, 120°C and 150°C.

Results and Discussion

The SSITKA experiment shows a significantly increased number of active species when 3 wt.% Mo is added to the Pt/ZrO_2 catalyst. In particular the amount of N_2 forming intermediates is increased e.g. from 4,3 $\mu mol \cdot g^{-1}$ to 35,0 $\mu mol \cdot g^{-1}$ at 120°C, whereas the N_2O-generating species are barely affected.

Table 1. Ratio of active species (SSITKA) to available platinum sites (CO-TPD).

	90°C	**120°C**	**150°C**
Pt/ZrO_2	0,7 ±0,9	3,7 ±2,1	7,3 ±1,4
$Pt/3Mo/ZrO_2$	6,1 ±0,6	5,6 ±0,5	1,0 ±0,3

However, for both catalysts the number of active species exceeds the number of available Pt sites (Table 1), suggesting some adsorbates on the support are also involved in the H_2-deNO$_x$ reaction.

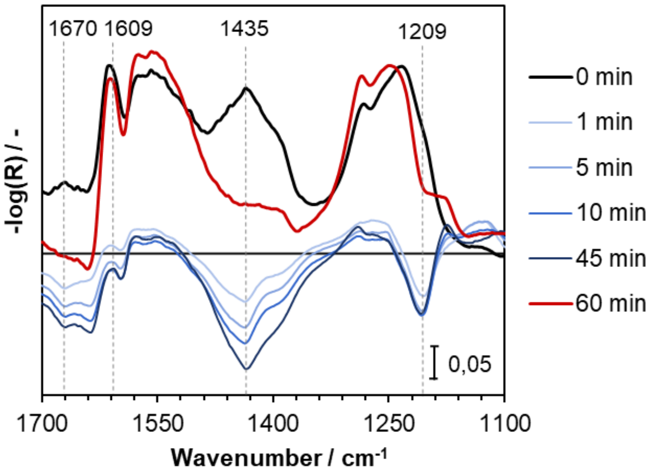

Figure 1. In-situ DRIFTS spectra of Pt/3Mo/ZrO_2 after H_2 to D_2 switch, Conditions: 200 ppm NO, 2000 ppm H_2/D_2, 5 Vol.% O_2, Ar Balance, ca. 70.000 h^{-1}.

In-situ DRIFTS experiments show that nitrites are active species on Pt/ZrO_2 as indicated by a 30 cm^{-1} red-shift of ν_{as}(N-O) band at 1190 cm^{-1}. It is assumed that active nitrites are reduced by hydrogen spillover from platinum particles [3]. Although up to 65 ppm NH_3 was detected in the gas phase, no evidence of active NH_x could be found on Pt/ZrO_2 after switch from H_2 to D_2.

In contrast using Pt/3Mo/ZrO_2 catalyst, no NH_3 is detected in the gas phase but in-situ DRIFTS experiments show characteristic bands of chemisorbed NH_3 (δ_{as}(NH_4^+) at 1435 cm^{-1} and δ_s(NH_3) at 1209 cm^{-1}). More importantly, H_2 to D_2 switch provides evidence that both NH_4^+ and NH_3 coordinated to Lewis acid sites are active for the NO_x reduction below 200°C even in the presence of H_2 (Fig. 1). The strong decline of δ_s(NH_3) band indicates the particularly high reactivity of NH_3 at the Lewis acid sites (Fig. 2). Additionally, nitrites also appear to be active species on Pt/3Mo/ZrO_2 catalyst. Note that the observed decline in IR band intensities of active species is in good agreement with the decay of ^{14}N product observed during SSITKA (Fig. 2).

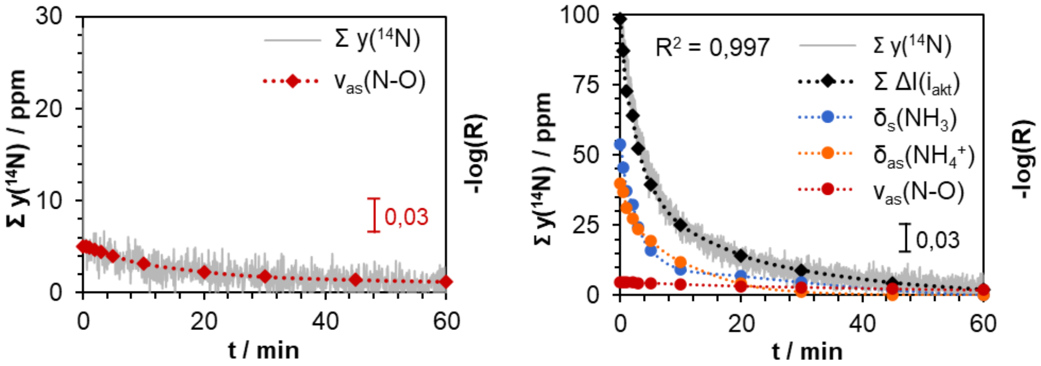

Figure 2. Decline of ^{14}N products (SSITKA) and band intensity of active species after switch from ^{14}NO to ^{15}NO and H_2 to D_2 (in-situ DRIFTS) at Pt/ZrO_2 (left) and Pt/3Mo/ZrO_2 (right) at 120°C.

The initial isotope distribution of the products reveals that NO_x reduction by NH_x species is a major reaction pathway for H_2-deNO$_x$ on the Mo promoted catalyst, accounting for about 70% of the total NO_x conversion at 120°C. Finally, initial selectivity of ^{14}N products demonstrates that the reaction of these active adsorbates mainly forms N_2 (S(N_2) > 80%).

The study proves for the first time that the of Pt/ZrO_2 with MoO_x enables an additional reaction pathway of H_2-deNO$_x$ with high N_2 selectivity. In this mechanism ammonia formed on the Pt sites readsorbs on the strong acid sites at highly dispersed MoO_x moieties, followed by a reaction of both NH_3 and NH_4^+ with NO at the interface between the Pt sites and MoO_x. Thus, our study highlights the particular importance of acidity to improve the activity and selectivity of lean H_2-deNO$_x$ catalysts.

References

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