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Preparation of Supported Pt-M Catalysts (M=Mo and W) from Anion-exchanged Hydrotalcites and their Catalytic Activity for Low Temperature NO-H₂-O₂ Reaction

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Preparation of Pt-Mo and Pt-W Catalysts from Anion-coexchanged Hydrotalcites

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Abstract

The NO-H\textsubscript{2}-O\textsubscript{2} reaction was studied over supported bimetallic catalysts, Pt-Mo and Pt-W, which were prepared by coexchange of hydrotalcite-like Mg-Al double layered hydroxides by Pt(NO\textsubscript{2})\textsubscript{4}\textsuperscript{2-}, MoO\textsubscript{4}\textsuperscript{2-}, and/or WO\textsubscript{4}\textsuperscript{2-} and subsequent heating at 600 °C in H\textsubscript{2}. The Pt-Mo interaction could obviously be seen when the catalyst after reduction treatment was exposed to a mixture of NO and H\textsubscript{2} in the absence of O\textsubscript{2}. The Pt-HT catalyst showed the almost complete NO conversion at 70 °C, whereas the Pt-Mo-HT showed a negligible conversion. Upon exposure to O\textsubscript{2}, however, Pt-Mo-HT exhibited the NO conversion at the lowest temperature of ≥30 °C, compared to ≥60 °C required for Pt-HT. EXAFS/XANES, XPS and IR results suggested that the role of Mo is very sensitive to the oxidation state, \textit{i.e.}, oxidized Mo species residing in Pt particles are postulated to retard the oxidative adsorption of NO as NO\textsubscript{3} and promote the catalytic conversion of NO to N\textsubscript{2}O at low temperatures.

Key words: NO-H\textsubscript{2}-O\textsubscript{2} reaction, Platinum, Molybdenum, Hydrotalcite
1. Introduction

Catalytic NO-H\(_2\) reactions in the presence of excess O\(_2\) have been investigated using Pt catalysts supported on various oxides [1-9]. However, the higher selectivity to N\(_2\)O rather than N\(_2\) would devalue the advantage of the lower reaction temperature (\(\leq 100\) °C) of these catalysts, because increasing attention is given in avoiding the formation of this effective greenhouse gas. One possible way to improve the N\(_2\) selectivity is the modification by promoters. Yokota et al. [1] reported that the N\(_2\) selectivity of Pt/SiO\(_2\) in the NO-H\(_2\)-O\(_2\) reaction was increased by the addition of Na and Mo, which would suppress the oxidation of Pt even in the presence of excess O\(_2\). We have previously reported that oxide supports having both moderate acidic and basic sites are requested for better N\(_2\) selectivity compared to acidic oxide supports like SiO\(_2\) and zeolites [6-9]. Pt supported on TiO\(_2\)-ZrO\(_2\) exhibited the higher selectivity to N\(_2\) rather than N\(_2\)O [6,8]. The addition of Na as a Lewis base to Pt-ZSM5 improved the N\(_2\) selectivity [8], because Na promotes the oxidative adsorption of NO as NO\(_2\)-type species, which would play a role of an intermediate to yield N\(_2\).

On this concern, Mg-Al oxides formed from hydrotalcite-like double layered hydroxides (HT) are promising because of their acid/base sites formed in the porous structure with a large surface area [10-12]. The thermal decomposition of Pt complex-exchanged hydrotalcites (Pt-HT) yields highly-dispersed Pt catalysts efficient for this reaction [13-15]. In the present study, supported bimetallic catalysts, Pt-M/Mg-Al-O (M=Mo and W), were prepared by coexchange of HT to apply for the low temperature NO-H\(_2\)-O\(_2\) reaction. The effect of additives (Mo and W) on the catalytic activity and selectivity of Pt was studied from structural and chemical view points.
2. Experimental

2.1 Catalyst preparation

A hydrotalcite-like compound, $\text{Mg}_{0.74}\text{Al}_{0.26}(\text{OH})_2(\text{NO}_3)_{0.26}\cdot n\text{H}_2\text{O}$, was prepared by the co-precipitation method [13]. $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (14.8 mmol) and $\text{Al(NO}_3)_3\cdot 9\text{H}_2\text{O}$ (5.2 mmol) were dissolved into a distilled water (20 mL) and resulting mixed solution was added dropwise into $\text{NH}_3$ aqueous solution (1 M, 100 mL) with vigorous stirring at room temperature. The precipitate was centrifuged, washed with distilled water and then dried under reduced pressure overnight. The powder thus obtained (HT) was exchanged in aqueous solutions of $\text{K}_2\text{Pt(NO}_2)_4$ at room temperature for 24 h to obtain $\text{Pt(NO}_2)_4^{2-}$-exchanged HT, which are abbreviated as Pt-HT. For the preparation of Pt-M coexchanged HTs (Pt-M-HT, M=Mo and W), mixed aqueous solutions of $\text{K}_2\text{Pt(NO}_2)_4$ and $\text{K}_2\text{MoO}_4$ or $\text{K}_2\text{WO}_4$ were used. As exchanged phases were washed with distilled water, dried under reduced pressure and heated at 600 °C in a flow of $\text{H}_2$ for 2 h to yield 1 wt% Pt and 0-10 wt% M-loaded catalysts.

2.2 Characterization

Unless otherwise stated, Pt-M-HTs with 1wt% Mo and 5wt% W loading were used for characterization. Crystal phases were determined by powder X-ray diffraction (XRD, Rigaku Multiflex) using monochromated Cu$K_\alpha$ radiation (30 kV, 30 mA). Chemical composition of as prepared catalysts was determined by an energy disperse X-ray fluorescence measurement (Horiba MESA-500W). Specific surface area was calculated by BET method from $\text{N}_2$ adsorption isotherm measured at 77 K (Belsorp-mini). The microstructure was observed by TEM (JEOL 2000FX, 200 kV). X-ray photoelectron
spectroscopy (XPS) spectra were measured on a VG Sigmaprobe spectrometer using AlK$_\alpha$ radiation (15 kV, 7 mA). The charging effect of XPS spectra was carefully corrected with adventitious carbon at 284.5 eV as a reference.

Pt L$_{III}$-edge XAFS spectra were recorded at BL-10B station of Photon Factory, High Energy Accelerator Research Organization at Tsukuba (Proposal #2004G088) using a Si(311) channel-cut monochromator. Injection beam energy was 2.5 GeV and ring current was 300-450 mA. Pt L$_{III}$-edge spectra were recorded at room temperature in a transmission mode using the ionization chambers filled with the detector gasses of Ar/N$_2$ (Ar/N$_2$=15/85) for the incident beam and of Ar for the transmitted beam, respectively. A sample was pressed into a disk after sample volume was adjusted by polyethylene powder to give appropriate absorbance at the edge energy for the XAFS measurement. After drying under reduced pressure overnight, the disk packed into a polyethylene package under Ar atmosphere. The XAFS data were processed by a REX 2000 (Rigaku) program assembly. The EXAFS oscillation is extracted by fitting a cubic spline function through the post edge region. In order to extract the amplitude and phase shift function for Pt–N, Pt–O, and Pt–Pt, K$_2$Pt(NO$_2$)$_4$, PtO$_2$ and Pt foil were used as reference. XANES spectra were normalized at the absorbance of 11575.5 eV. The integrated white line intensity in the XANES spectrum was calculated in the range of 11513.6-11575.5 eV and was normalized by the value obtained from the Pt foil.

2.3 Adsorption and catalytic measurement

NO adsorption was measured in a conventional flow reactor equipped with a water-cooled infrared image furnace. A granulated catalyst (10-20 mesh, 0.2 g) was fixed by quartz wool in a Pyrex glass tube (4mm I.D.). The catalyst was pretreated at 400 °C in 5% H$_2$/He flow
for 1h before use. Breakthrough curves of NO\textsubscript{x} adsorption were measured in a flowing gaseous mixture of 0.16% NO, 10% O\textsubscript{2}, balanced with He supplied at 0.24 s\cdot g\cdot cm\textsuperscript{-3}. The concentration of NO\textsubscript{x} (NO+NO\textsubscript{2}) in the effluent was measured by using a chemiluminescence NO\textsubscript{x} analyzer (Shimadzu NOA-7000). FT-IR spectra of NO\textsubscript{x} species adsorbed on catalysts were recorded on a Jasco FTIR-610 spectrometer equipped with a temperature-controllable diffuse reflectance reaction cell (Jasco DR600A) with a KBr window to allow in situ measurement under controlled gas environments at atmospheric pressure. The sample was treated in a stream of 5% H\textsubscript{2}/He at 400 °C for 1 h and subsequently cooled down to 50 °C. After purging with He for 30 minutes, gas mixtures of 0.16% NO, 10% O\textsubscript{2} balanced with He was admitted to the cell for 2 h. This was followed by spectra measurement of NO\textsubscript{x} adsorbates in a flowing He at 50 °C.

Catalytic NO-H\textsubscript{2}-O\textsubscript{2} reaction was also carried out in a conventional flow reactor. Prior to catalytic reactions, all the catalyst was preheated at 400 °C in a flow of 5% H\textsubscript{2}/He. A mixed gas consisting of 0.08% NO, 0 or 10% O\textsubscript{2}, 0.28% H\textsubscript{2}, balanced with He was supplied to the catalyst bed at W/F=0.24 s\cdot g\cdot cm\textsuperscript{-3}. Effluent gas was analyzed using a chemiluminescence NO\textsubscript{x} analyzer (Shimadzu NOA-7000) and a TCD gas chromatograph (Shimadzu GC-8A) with molecular sieve-5A and Porapak-Q columns.

3. Results and discussion

3.1 Structure and property of Pt-M-HT (M=Mo and W)

The XRD patterns of coexchanged Pt-M-HT (M=Mo and W) before calcination were very similar to that of pristine HT with a brucite-type layered structure. The change of interlayer distance could not be observed even in the case of large amounts of exchange (ca.3 % for
1wt% Pt and ca. 60% for 10wt% Mo loadings). However it was confirmed that the interlayer distance was increased slightly from 0.89 to 0.93 nm by the complete exchange (100% for 16.6wt% Mo loading). After heating at 600 °C in H₂, the layered structure was collapsed to yield an MgO-like phase with a low crystallinity. Figure 1 shows the BET surface area of as calcined Pt-M-HT catalysts with different loadings of M (1wt% Pt). A large surface area of Pt-HT (177 m²·g⁻¹) was due to the micropores and mesopores, which were created by the thermal decomposition of the HT phase [13-15]. With increasing addition of Mo or W, the surface area was decreased monotonically, but the shape of N₂ adsorption isotherms and TEM observation could not detect significant difference between Pt-HT and Pt-M-HT. The decreased surface area would therefore be due to the pore blockage caused by deposition of Mo and W oxides. The Pt dispersion of Pt-HT measured by the H₂-O₂ titration was 61%, but that of Pt-M-HT could not be determined by this method because consumptions of H₂-O₂ were negligible. The dispersion was therefore evaluated by TEM (Figure 2). In a micrograph of Pt-HT, Pt particles with a uniform size of around 2 nm were dispersed in the porous and amorphous-like matrix of Mg-Al oxides. This corresponds to the size of Pt that was estimated from the result of the H₂-O₂ titration (2.2 nm). Pt particles with almost the same size were also observed for Pt-Mo-HT (2 wt% Mo). Therefore, the apparent dispersion of Pt is not affected by the addition of Mo.

X-ray adsorption measurement was carried out to elucidate the electronic structure and chemical environment of Pt. Figure 3 shows normalized XANES at the Pt L₃₃-edge of Pt-HT and Pt-Mo-HT a) before and b) after heating at 600 °C in H₂ and subsequent exposure to air at room temperature. The white line at the Pt L₃₃-edge is an absorption threshold resonance attributed to the electronic transitions from 2p₃/2 to unoccupied states above the Fermi level and
is therefore intensified with an increase in the d-band vacancies as a result of oxidation. The white line absorption peak of Pt foil (Pt$^0$) at 11566.5 eV gave a lower intensity, whereas K$_2$Pt(NO$_2$)$_4$ (Pt$^{2+}$) yielded intensified peaks at a higher energy of 11568.4 eV. Table 1 summarizes the peak positions and the integrated intensity of white line normalized by using the spectrum of Pt foil. With regard to the area and peak position of white lines, as-exchanged Pt-HT and Pt-Mo-HT were very similar to K$_2$Pt(NO$_2$)$_4$ (Pt$^{2+}$), whereas Pt-HT after heating at 600 °C in H$_2$ and Pt foil (Pt$^0$) were almost the same. However, Pt-Mo-HT after heating at 600 °C in H$_2$ exhibited the increase in the area and shift of peak position to high energy as compared with Pt-HT. The peak position for Pt-Mo-HT (11567.2 eV) was intermediate between that of Pt foil (11566.5 eV) and K$_2$Pt(NO$_2$)$_4$ (11568.4 eV). These results suggest that a part of Pt species near the surface of Pt-Mo-HT was oxidized. The XPS spectra of Mo3d$_{5/2}$ exhibited signals due to Mo$^{6+}$ (232.5 eV) and Mo$^{4+}$ (229.8 eV) but negligible amount of Mo$^0$ (228.1 eV). These oxidized species of Pt and Mo would be created when the samples were exposed to air at room temperature after the reduction treatment.

Figure 4 shows the Fourier transforms of $k^3$-weighted Pt L$_{III}$-edge EXAFS for Pt-HT and Pt-Mo-HT as exchanged and after heating at 600 °C in H$_2$. The EXAFS spectra of as-exchanged Pt-HT and Pt-Mo-HT were very similar, suggesting that the Pt species in both samples have the same local structure. Judging from the reference spectra of K$_2$Pt(NO$_2$)$_4$, the two peaks at around 0.20 nm and 0.28 nm are attributed to the Pt-N and Pt-N-O bonds, respectively. The EXAFS spectra of Pt-HT after heating at 600 °C in H$_2$ showed a Pt–Pt peak at around 0.28 nm due to metallic Pt particles. By contrast, Pt-Mo-HT exhibited a very weak peak at this distance although the TEM images proved that the Pt particles with almost same size were observed in both samples (Figure 2). It has been reported that supported Pt clusters
with the same size often give different intensities of the Pt–Pt EXAFS peak when adsorption of molecules and/or interaction with oxide supports affected the Debye-Waller factor [16,17]. In the present Pt-Mo-HT catalyst, the interaction between Pt and Mo-O$_x$ species is supposed to cause the disorder of Pt-Pt shell. Similarly, the absence of Pt-O band is probably due to the lack of short periodicity of the local structure surrounding Pt, which results in the significant decrease in EXAFS oscillation.

3.2 Catalytic properties of Pt-M-HT (M=Mo and W) for NO-H$_2$-O$_2$ reaction

The catalytic activity of Pt-M-HT (M=Mo and W) for the NO-H$_2$-O$_2$ reaction was evaluated after pretreatment in 5% H$_2$/He at 400 °C. Figures 5 and 6 show the temperature dependences of NO$_x$ conversion and N$_2$ selectivity of Pt-M-HT with different loading of M. The NO$_x$ conversion over Pt-HT was initiated at $\leq$50 °C and increased with an increase of the temperature. The maximum activity was observed at 70 °C, where the NO$_x$ conversion of 83 % and the N$_2$ selectivity of 53 % were attained. Further increase of the reaction temperature led to the monotonous decrease of NO$_x$ conversion, because NO and O$_2$ compete to react with H$_2$. Addition of Mo up to 2 wt% improved the NO$_x$ conversion at low temperature of $<$70 °C. The reaction over 1wt% Pt-2wt% Mo-HT could already be initiated at as low as 30 °C, compared to $\geq$50 °C requested for the pristine Pt-HT. However, further increase of the Mo loading caused the deactivation at lower temperatures and thus shifted the maximal NO conversion toward higher temperatures ($\geq$80 °C). The addition of W also caused the improved NO conversion up to 5wt%-loading, but the effect was less obvious. The deactivation at high loading of Mo and W would be associated with the oxidation state of Pt. As mentioned above, the addition of Mo/W yielded oxidized Pt (Pt$^{2+}$) relative to Pt metal presumably because of the interaction with these additive oxides. At high loading of Mo/W, the fraction of oxidized Pt
should be very high. According to our previous study [6], the activity of supported Pt for NO-H\textsubscript{2}-O\textsubscript{2} reaction is sensitive to the oxidation treatment. Pt catalysts after total oxidation treatment showed the lower activity rather than those after reduction treatment. Thus, highly oxidized Pt surface caused by high loading of Mo/W may be a reason for the decreased catalytic activity. The N\textsubscript{2} selectivity of Pt-HT was decreased with an increase of M in a whole temperature range (Figure 6). This trend was more obvious at lower temperatures (\leq 50 °C) and for the catalysts with higher loadings of M.

To confirm the difference of catalytic property between Pt-HT and Pt-Mo-HT, the catalysts were placed in different gas mixtures after pretreatment in 5% H\textsubscript{2}/He at 400 °C. Figure 7 shows the effluent NO\textsubscript{x} concentration profiles from (a) Pt-HT and (b) Pt-Mo-HT (2wt% Mo) catalysts at 70 °C. A most noticeable difference was observed in a flowing mixture of 0.08% NO, 0.28% H\textsubscript{2} and He balance (region I), i.e., Pt-HT exhibited almost complete NO conversion, whereas the conversion for Pt-Mo-HT was less than 15%. Generally, a supported Pt catalyst is highly active for NO-H\textsubscript{2} reactions even at room temperature. The result is therefore indicative of significant alternation of Pt surface probably due to the formation of Pt-Mo intermetallic phases after the treatment in H\textsubscript{2}. When the gas feed was switched to a mixture of 0.08% NO, 0.28% H\textsubscript{2}, 10% O\textsubscript{2} and He balance (region II), the NO conversion over Pt-Mo-HT increased drastically to exceed 95%, whereas the activity of Pt-HT was slightly decreased to ca. 92%. Although the gas feed was returned to NO-H\textsubscript{2}-He (region III), the high activity of Pt-Mo-HT was retained, suggesting that the active site was generated by the exposure to O\textsubscript{2} in region II. Various intermetallic phases are known for the Pt-Mo system [18,19], but we could not determine the actual phase in Pt-Mo-HT by XRD measurement in air. These results suggest that the inactive metallic Pt-Mo phase should be unstable in air and oxidized immediately by O\textsubscript{2}. 
to form the active site for NO-H$_2$ reaction. This can be supported by the XPS spectra of Mo3d$_{5/2}$, which exhibited the presence of Mo$^{6+}$ and Mo$^{4+}$. Similarly, W$^{6+}$ and W$^{4+}$ species were observed for the Pt-W-HT catalyst.

The NO adsorption onto the catalysts was determined from breakthrough curves measured in a flow of 0.16% NO, 10% O$_2$ and He balance at 70 °C. Irrespective of the smaller surface area, Pt-Mo-HT (1wt% Mo) showed a larger NO uptake, 0.18 mmol·g$^{-1}$, compared to that for Pt-HT, 0.10 mmol·g$^{-1}$. The NO adsorption increased with an increase of the Mo loading. The NO uptake is believed to result from the basicity of Mg-Al oxides, which is favorable for the oxidative adsorption of NO in the presence of O$_2$. However, the acidic oxides of Mo should not be suitable for such oxidative NO adsorption. This means that the addition of Mo should yield the different NO adsorption species.

To analyze NO$_x$ species adsorbed on the catalyst, in situ DRIFT spectra were recorded after treatment in a stream of NO-O$_2$ mixture at 50 °C (Figure 8). All the spectra were referenced to that of the sample in flowing He just before exposure to NO. The adsorbed species formed on the Pt-HT were assigned to nitrite (NO$_2$, ca.1350 cm$^{-1}$) and nitrate (NO$_3$, ca.1640, 1500 and 1300 cm$^{-1}$) according to those reported previously [20-22]. In case of Pt-M-HT, a peak due to NO$_2$ became much more intense, whereas those due to NO$_3$ became weak. This suggested that the addition of Mo and W suppress the oxidation of NO to NO$_3$, probably because of their acidic character. These results suggest the addition of acidic oxide, Mo/W, would decrease the strength of base site on Mg-Al oxides, but the number of base site would be kept almost constant. The NO adsorption onto MoO$_x$ is reported to form NO or (NO)$_2$-type species [23], but these nitrosyl species were not observed in the present work.

We have previously reported that catalytic NO-H$_2$-O$_2$ reaction is affected by acidic/basic
characters of oxide supports [6-9]. Although acidic and/or amphoteric oxides (SiO$_2$, ZrO$_2$, Al$_2$O$_3$, ZSM-5, SiO$_2$-Al$_2$O$_3$, TiO$_2$-ZrO$_2$, etc.) are rather effective for the NO reduction at lower temperatures, considerably more N$_2$O than N$_2$ is produced. According to the mechanism proposed by Burch and Coleman [5], the formation of N$_2$O in the NO-H$_2$-O$_2$ mixture forms as follows,

$$\text{NO}_{\text{ad}} + \text{NO}_{\text{ad}} = \text{N}_2\text{O} + \text{O}_{\text{ad}}$$

In the present system, such NO-type adsorption species are not detected by infrared spectra. NO adsorbed as NO$_2$/NO$_3$ would monopolize Pt surface and this is a reason why simple H$_2$-O$_2$ reaction is severely inhibited at lower temperatures. However, the addition of Mo or W to Pt-HT would suppress such oxidative adsorption as NO$_3$ because of the acidic character of their oxides (MoO$_x$ and WO$_x$), so that the formation of NO-type species would be possible under the reaction atmosphere. The NO$_3$ adsorbents with lower oxidation states must be rather reactive toward H$_2$, compared to thermodynamically stable NO$_3$ species. This is consistent with higher NO conversion of Pt-Mo-HT and Pt-W-HT at lower reaction temperatures.

4. Conclusion

The supported Pt-Mo and Pt-W catalysts were prepared from coexchanged Mg-Al hydrotalcite-like double layered hydroxides. After reduction treatment in H$_2$, the Pt surface would form an intermetallic Pt-Mo phase that is inactive for NO-H$_2$ reaction. However, the Pt-Mo phase is easily oxidized to Pt-Mo-O$_x$ species in the presence of O$_2$, which exhibited very high catalytic activities for the NO-H$_2$-O$_2$ reaction at low temperature of 40 °C. The reaction at such low temperature is selective toward N$_2$O rather than N$_2$.
Acknowledgement

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References


Table 1  Results of Pt L_{III} edge XANES analysis

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<td>11568.4</td>
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<td>11567.2</td>
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a) Ratio of integrated white line intensity for samples to that for Pt foil,

b) Central position of white line peak.
Figure 1. BET surface area of 1wt%Pt-Xwt%M-HT (X=0-10, M=Mo and W).

Figure 2. TEM images of a) Pt-HT and b) Pt-Mo-HT after heating at 600 °C in H₂.

Figure 3. Normalized Pt L₃-edge XANES spectra with energy offset at 11562eV.
a) as exchanged, b) after heating at 600 °C in H₂.
Figure 4. Fourier transforms of $k^2$-weighted Pt L<sub>III</sub>-edge EXAFS.

a) as exchanged, b) after heating at 600 °C in H<sub>2</sub>.

Figure 5. NO<sub>x</sub> conversion of 1wt%Pt-Xwt%M-HT (X=0~10, M=Mo and W).

0.08%NO, 0.28%H<sub>2</sub>, 10%O<sub>2</sub>, He balance, W/F=0.24 s·g·cm<sup>-3</sup>.
Figure 6. $N_2$ selectivity of 1wt%Pt-Xwt%M-HT (X=0~10, M=Mo and W).

0.08%NO, 0.28%H$_2$, 10%O$_2$, He balance, W/F=0.24 s·g·cm$^{-3}$. 
Figure 7. Effluent NO$_x$ concentration of a) Pt-HT and b) Pt-Mo-HT at 70 °C.

I) 0.08%NO, 0.28%H$_2$, He balance, W/F=0.24 s·g·cm$^{-3}$,

II) 0.08%NO, 0.28%H$_2$, 10%O$_2$, He balance, W/F=0.24 s·g·cm$^{-3}$,

III) 0.08%NO, 0.28%H$_2$, He balance, W/F=0.24 s·g·cm$^{-3}$,

IV) 0.08%NO, He balance, W/F=0.24 s·g·cm$^{-3}$.

Figure 8. In situ DRIFTS of adsorbed NO$_x$ measured in a flowing mixture of 0.16%NO, 10%O$_2$, He balance at 50 °C.