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Pillared smectite modified with carbon and manganese as catalyst for SCR of NO_x with NH_3.
Part II. Temperature-programmed studies

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Temperature-programmed desorption (TPD) and surface reaction (TPSR), and additionally FTIR spectroscopy of adsorbed NO molecules were used to characterise surface sites on pillared smectites modified with carbon and manganese. Much higher adsorption of NH_3 than NO was found, but acidic pre-treatment increased NO sorption to comparable values as well as catalytic performance in SCR of NO_x. In this case formation of strongly bound NO_3^- species was recognised, which reacted with NH_3 at a temperature 200 °C higher than weaker adsorbed NO.

Keywords: SCR of NO_x, zirconia pillared smectites, carbon deposits, manganese oxides, TPD, TPSR

1. Introduction

As reported in a previous paper [1], a series of zirconia-pillared smectites modified with carbon and manganese was prepared and used as catalysts for SCR of NO with ammonia. The idea to prepare and test such catalysts arose from another previous study on transition metal oxides supported on active carbons [2]. Active carbons promoted with transition metal oxides were found to catalyse NO_x reduction at temperatures below 300 °C [3,4], but their low mechanical and thermal stability preclude their commercial application. Since active carbons have a great number of small micropores, which are inaccessible to reacting molecules, it seemed promising to apply a support showing easier accessable pore structure. The pillared smectites were chosen because of their large surface area, high mechanical durability and resistance to SO_x poisoning [5].

Our activity studies [1], which were performed in a plug-flow reactor under steady state conditions, showed that zirconia-pillared smectites are active and selective catalysts for the DeNOx process. The highest activity was found for catalysts prepared from acid pre-treated smectites modified with carbon and manganese. The present paper is devoted to an additional characterisation of these catalysts using temperature-programmed methods (NH_3-TPD, NO-TPD and TPSR) supported by FTIR spectroscopy of pre-adsorbed NO molecules.

2. Experimental

2.1. Samples

Smectite obtained by sedimentation from natural bentonite from Jelsowy Potok (Slovakia) was used as a raw material for the preparation of the catalysts. A part of it was pre-treated with 20% HCl. The samples were pillared by impregnation with zirconia oligocations and calcined at temperature up to 500 °C. The pillared materials were contacted with water solution of polyacryloamide (Gigtar) and subsequently carbonised at 500 °C. Both carbon-modified and unmodified samples were promoted by adsorption methods with Mn cations and calcined. Thus prepared catalysts were stable in both pure helium as well as oxygen-containing atmosphere up to 500 °C. The list of the samples with the respective notation is presented in table 1.

The surface and bulk composition, structure and texture of the obtained materials were earlier characterised by XPS,

Table 1
List of the samples.

Catalysts code	Sample preparation
M1	Zirconia-pillared smectite
M2	Acid-treated zirconia-pillared smectite
M1Mn0.7	M1 promoted with Mn cations (0.7 wt%)
M1C	M1 modified with carbon deposit
M2C	M2 modified with carbon deposit
M1CMn16	M1C promoted with Mn cations (16 wt%)
M2CMn14	M2C promoted with Mn cations (14 wt%)

XRF, XRD and Ar adsorption. Details of both samples preparation and characterisation can be found elsewhere [1].

2.2. Temperature-programmed desorption (TPD)

The TPD of NH_3 or NO was carried out in the range 70–500 °C in a fixed-bed continuous-flow quartz microreactor (i.d. 4.5 mm, length 240 mm). The temperature in the catalyst bed was measured by a K-type thermocouple located in a quartz capillary immersed in the catalyst bed. The molecules desorbing from the samples were monitored on-line by a quadrupole mass spectrometer (VG SX 200) connected to the reactor outlet by a heated line.

Before TPD experiments the smectite samples (70 mg) were outgassed in a linear temperature program ($\beta = 10\,^{\circ}$C/min) up to 450 °C in flow of helium (25 Ncm^3/min). Subsequently the samples were cooled down to 70 °C and saturated for about 30 min in 1% NH_3/He or 1% NO/He (25 Ncm^3/min). Subsequently the samples were purged in the He carrier flow until a constant baseline level was attained. Desorption was carried out with linear heating rate ($\beta = 10\,^{\circ}$C/min) in a flow of He (25 Ncm^3/min). Traces of H_2O and O_2 in pure helium (grade 5) used as the eluent gas were removed by appropriate traps (Alltech). The NH_3- and NO-TPD spectra were obtained, respectively, from the $m/z = 16$ and 30 mass-to-charge signal ratios. Appropriate commercial gas mixtures were used to recalculate the QMS signal to concentration of a given product and then, to desorption or reaction rate.

2.3. NH_3-TPSR (temperature-programmed surface reactions)

After outgassing the sample was exposed to ammonia according to the procedure applied in NH_3-TPD. In the next step the reactor was purged in a flow of helium and then the catalyst was heated up to about 520 °C with a linear increase of temperature ($\beta = 10\,^{\circ}$C/min) in a flow of gas mixture containing 0.5% NO and 2.5% O_2 (25 Ncm^3/min).

2.4. NO-TPSR

Before NO-TPSR experiments the sample was outgassed and cooled down according to the procedure applied in NO-TPD. Subsequently it was saturated at 70 °C for 30 min with a gas mixture containing 0.5% NO and 2.5% O_2 in He (total flow 40 Ncm^3/min) and purged with helium until a constant base level was attained. Then the catalyst was heated up to about 480 °C in a flow of 1% NH_3/He (flow 25 Ncm^3/min) with linear increase of temperature ($\beta = 10\,^{\circ}$C/min).

2.5. Stop flow-TPD experiments

The catalytic tests were carried out at 253 °C with catalyst mass of 200 mg using a mixture containing 2500 ppm NO and NH_3, 2.5% O_2 and He as a balancing gas at a total flow rate of 40 Ncm^3/min lasting 1 h. Subsequently the flow of reacting gas mixture was exchanged for pure helium. The catalyst was purged in the He carrier flow until a constant baseline level was attained. Afterwards TPD was carried out with a linear heating rate of 10 °C/min in a flow of He (25 Ncm^3/min) up to 450 °C.

3. Results and discussion

3.1. NH_3-TPD

The NH_3-TPD profiles of the modified smectites are shown in figure 1. Sorption of ammonia has been performed at a temperature of 70 °C, which is high enough to avoid formation of physisorbed ammonia complexes on the catalyst's surface. NH_3-TPD spectra obtained for studied smectites are characterised by broad, asymmetric desorption patterns, spanned in the temperature range of 100–500 °C with the maximum at about 175 °C. In the case of both M2CMn14 and M2 catalysts the main desorption maxima are shifted to 225 °C. The rate of desorption increased sharply from about 100 °C and after reaching the maximum slowly decreased. In the case of sample M2C a few small desorption maxima appeared on the high temperature side of the main peak. However, it was impossible to distinguish various adsorption sites and only their total amount was calculated. The amount of the desorbed ammonia, its surface concentration and the coverage of catalysts' surface by a monolayer of ammonia are gathered in table 2. For all samples, with the exception of M1CMn16, the quantity of sorbed NH_3 was above 200 μmol/g. These values respond to only a few percent of NH_3 monolayer coverage.

3.2. NO-TPD

The NO-TPD patterns of the studied samples are shown in figure 2, while both the amount of desorbed NO and

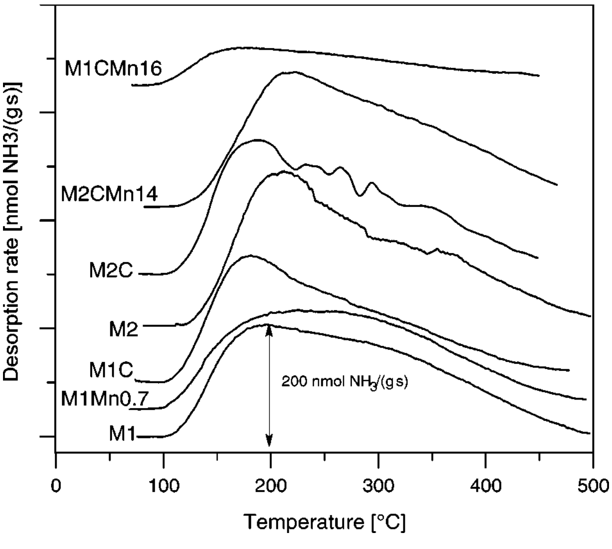

Figure 1. NH_3-TPD profiles of zirconia-pillared smectites modified with carbon and manganese.

Table 2
Amount of sorbed NH_3, its surface concentration and coverage of catalysts' surface by monolayer of ammonia.

Catalyst	Amount of sorbed NH_3 (μmol/g)	Surface concentration of NH_3 (μmol/m^2)	Coverage of surface by monolayer of NH_3[a] (%)
M1	211.7	0.7	6.3
M2	339.1	1.1	9.9
M1Mn0.7	200.3	0.6	5.4
M1C	262.6	1.4	12.6
M2C	291.2	1.0	9.0
M1CMn16	94.5	0.5	4.5
M2CMn14	251.8	1.3	11.7

[a] The area covered by one ammonia molecule determined according to the van der Waals' model assumed in calculations is 15 Å^2 [10].

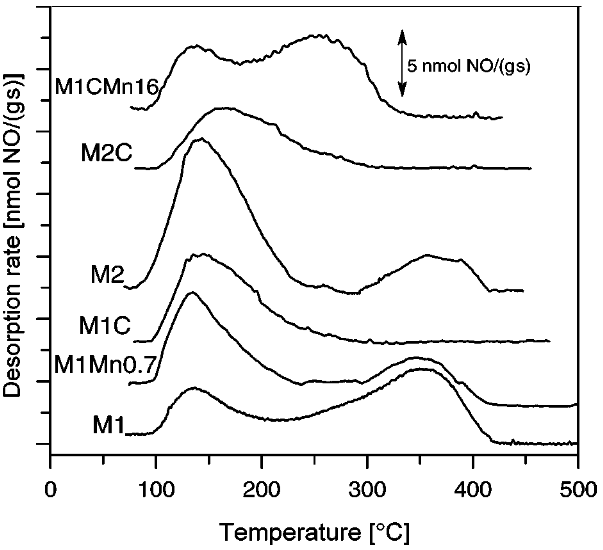

Figure 2. NO-TPD profiles of zirconia-pillared smectites modified with carbon and manganese.

Table 3
Amount of sorbed NO and its surface concentration.

Catalyst	Amount of sorbed NO (μmol/g)	Surface concentration of NO (μmol/m^2)
M1	4.9	0.02
M2	5.2	0.02
M1Mn0.7	5.3	0.02
M1C	4.0	0.02
M2C	3.1	0.01
M1CMn16	6.6	0.04
M2CMn14[a]	395.2	2.09

[a] In this case formation of NO_3^- was detected. Gaseous products of nitrates decomposed were NO, N_2O, NO_2 and O_2.

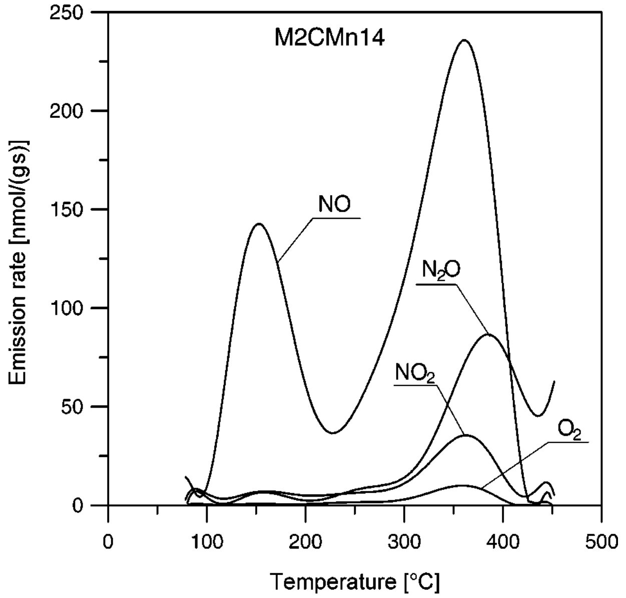

Figure 3. Profiles of NO_x and O_2 emissions obtained after NO sorption on the M2CMn14 catalyst.

its surface concentration are summarised in table 3. They are nearly two orders of magnitude smaller than those obtained in NH_3-TPD experiments. The NO-TPD spectra are characterised by well-resolved peaks. Two desorption maxima (140 and 360 °C) were detected for zirconia-pillared smectites (M1 and M2). Carbon deposits introduced into these materials selectively blocked some NO sorption sites resulting in a disappearance of the high-temperature peak (compare M1C and M2C with M1 and M2). Such a change of desorption spectra in comparison with texture parameters [1] suggests that the strongest NO sorption sites are located inside the micropores. The introduction of manganese into pillared smectite (M1Mn0.7) or pillared smectite modified with carbon (M1CMn16) resulted in formation of new NO sorption sites with medium strength.

Totally different results were obtained for the M2CMn14 sample (figure 3). In this case not only desorption of NO but also the emission of N_2O, NO_2 and O_2 was observed. Additionally, the total amount of emitted nitrogen oxides (NO_x) was two orders of magnitude higher than those obtained for the other samples and amounted to 334.3 μmol/g, of which NO, N_2O and NO_2 amounted to, respectively, 266.8, 61.4 and 6.1 μmol/g. The spectrum of NO emission is characterised by two symmetric and well-resolved peaks at 155 and 360 °C, respectively. Emission of N_2O, NO_2 and O_2 occurred mainly at temperatures above 250 °C with main peaks in the temperature range of 350–400 °C, although small amounts of N_2O and O_2 were also produced at lower temperature. Emission of CO_2 was excluded concluding from the observed ratio of 44–14 mass-to-charge signals.

In order to identify the way of NO bonding with catalyst surface, the sample before and after NO sorption was moved into an FTIR spectrometer (Bruker IFS 48) and infrared spectra were recorded (1% of sample in KBr). Both FTIR spectra are shown in figure 4. NO sorption results in the formation of a distinct maximum at 1385 cm^{-1} which can be ascribed to the presence of NO_3^- anions [6]. Kapteijn et al. [7] suggest that NO is sorbed preferentially on Lewis basic surface oxygen ions. Adsorbed NO molecules may be oxidised to NO_2 or nitrito or nitrate groups which have stronger interaction with the catalyst surface

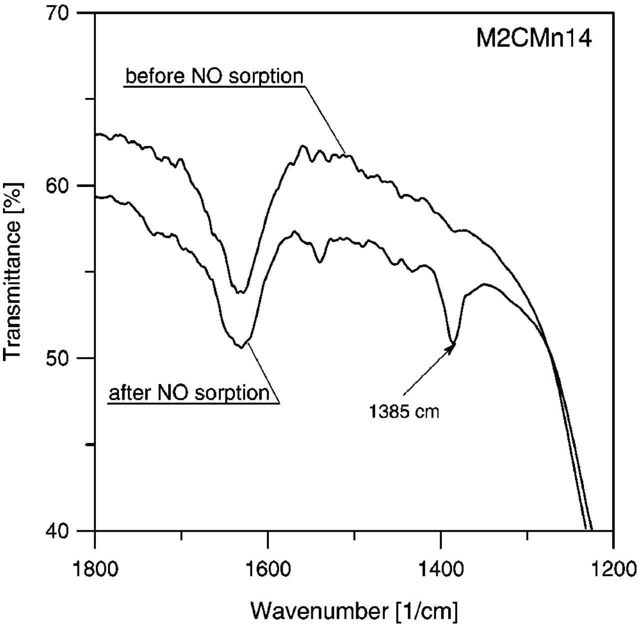

Figure 4. FT-IR spectra obtained for the outgassed M2CMn14 sample and for this sample after NO sorption.

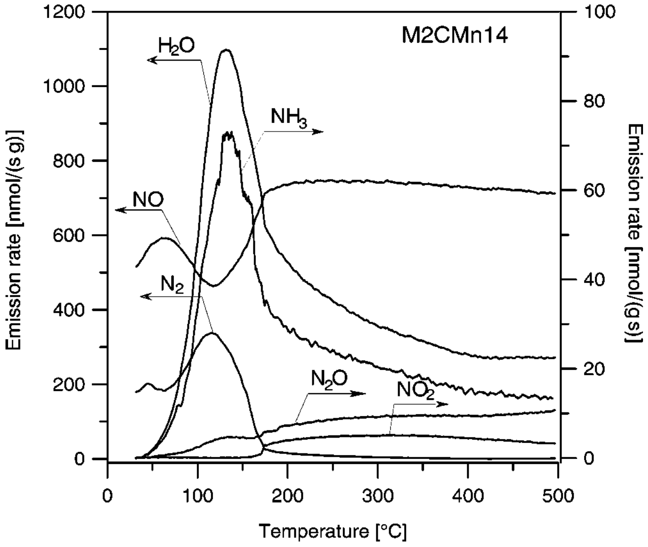

Figure 5. NH_3-TPSR profiles for the M2CMn14 catalyst.

than NO. Such effect was found for a MnO_x–ZrO_2 system by Eguchi et al. [6] who proposed the following mechanism for this process: MnO_x supplies the lattice oxygen which oxidises adsorbed NO to form nitrates bound by basic zirconia oxide. Then, reduced Mn ions are reoxidised by oxygen from the gas phase. According to this mechanism, oxidation of NO to NO_3^- proceeds in the presence of oxygen while in the present study both sorption and desorption of NO were carried out in oxygen-free atmosphere. For this reason the amount of formed NO_3^- anions was limited by the number of oxygen atoms supplied by manganese oxide. To perform respective calculations the exact form of mangania should be known. Our attempts to measure the oxidation state of Mn by XPS failed because there are not enough Mn ions on the surface of the catalyst and most of them are probably present in the micropores of the sample. Grzybek et al. [8] showed that thermal decomposition of $Mn(NO_3)_2$ on an active carbon surface leads to Mn_3O_4, Panayotov [9] observed a formation of the same Mn oxide during calcination of γ-Al_2O_3 impregnated with $Mn(NO_3)_2$ solution. On the basis of the measured amount of NO_x produced during thermal decomposition of nitrates and the amount of manganese introduced as the assumed Mn_3O_4 for the sample M2CMn14, it may be estimated that about 93% of Mn_3O_4 was reduced to MnO by NO.

The formation of nitrates was detected only in the case of acid-treated catalyst M2CMn14 while there were two other Mn-containing catalysts (M1Mn0.7 and M1CMn16). If the formation of nitrates during sorption of NO depends on the oxidation state of mangania, then the carbon content may play an important role due to its reducing properties. The sample M1CMn16 contains twice as much carbon as M2CMn14 (0.54 and 0.25 wt%, respectively) but the total amount of mangania in the case of both catalysts is much higher than the C-content and Mn_3O_4 cannot be reduced to a larger extent. Moreover, the production of CO_x was not observed during the calcination of the sample M1CMn16 and its additional oxidation at 200 °C performed before NO sorption does not lead to the formation of nitrates. So this mechanism must be rejected.

The other essential difference between acid-treated and untreated pillared smectites is their textural properties [1]. Acid-treated pillared smectite contains both micro- and mesopores, while untreated material contains mainly micropores. It seems possible that nitrates bound to zirconia pillars produced during NO sorption block access to micropores and make it impossible to form larger amounts of nitrates. For the mesopores this effect should not occur and thus the amount of produced nitrates would be much higher.

Because nitrates are formed for the most active catalyst, we should ask the question whether they are produced in the course of the DeNOx reaction and if yes, whether there is a connection between this fact and the high activity of M2CMn14. In order to solve these problems TPSR and "stop flow–TPD" experiments have been carried out.

3.3. TPSR

The reactivity of pre-adsorbed NH_3 was characterised by temperature-programmed surface reaction (NH_3-TPSR) performed in a continuous flow of helium-diluted NO. The NH_3-TPSR profiles of the M2CMn14 sample are shown in figure 5. The increase in ammonia desorption rate begins as early as at 70 °C reaching maximum at 150 °C (72 nmol/(g s)). Similar patterns were recorded for the emission of N_2 and H_2O and the maximum rate of their evolution reached much higher values (370 and 1100 nmol/(g s), respectively). Also the maximum of NO consumption is centred at the same temperature. Emission of a small amount of N_2O starts at 70 °C and increases thereafter while NO_2 evolution begins at 170 °C and stays

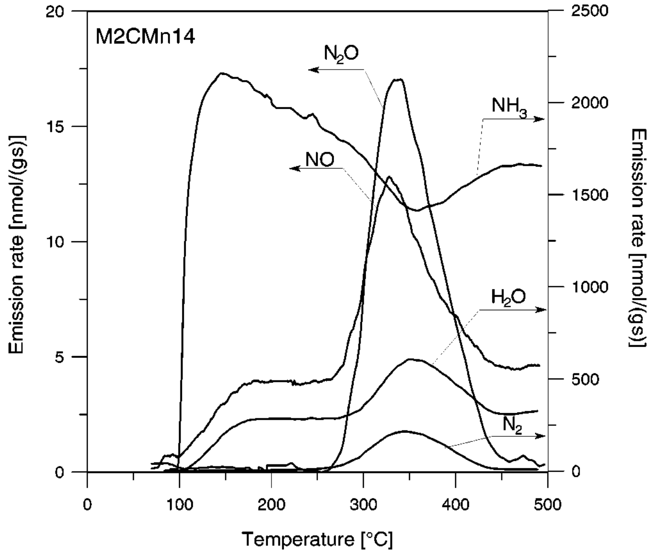

Figure 6. NO-TPSR profiles for the M2CMn14 catalyst.

nearly constant at low values up to the highest temperature studied (500 °C).

The NO-TPSR results obtained for the M2CMn14 sample are presented in figure 6. In spite of the pre-adsorbed NO the catalyst adsorbs all NH_3 from the effluent gas up to about 100 °C, but the small production of N_2 and H_2O begins just after introduction of NH_3 to the reactor. The main peak of N_2 evolution is characterised by a symmetric maximum centred at 340 °C. At the same temperature a maximum of ammonia consumption was observed. Emission of water starts at 100 °C and sharply increases reaching a plateau at 180 °C. The rate of H_2O evolution increases again at 280 °C reaching a maximum at 350 °C. Only very small amounts of NO and N_2O were detected.

TPSR experiments show that pre-adsorbed ammonia can be converted into DeNOx products at much lower temperature than the nitrates present on the catalyst surface. The nitrate species react above 280 °C when no weaker bond NO species are present on the surface because of earlier desorption (figure 6). So, it seems that two reaction paths are possible depending on the reaction temperature.

3.4. Stop flow–TPD experiments

The experiments were performed on the most active catalyst (M2CMn14) after 2 h time-on-stream and a further outgassing at a constant temperature of 253 °C. The evolution of H_2O and NH_3 from the catalyst surface was observed (figure 7) together with the formation of much smaller amounts of NO, directly after the beginning of the TPD run. The desorption spectra of NH_3 and NO are characterised by symmetric maxima centred at about 370 °C while desorption of water is very high also above this temperature.

The obtained results suggest that formation of NO_3^- anions on the catalyst surface needs co- or pre-adsorption of O_2. Probably ammonia sorbed on the catalyst surface hinders formation of NO_3^- ions.

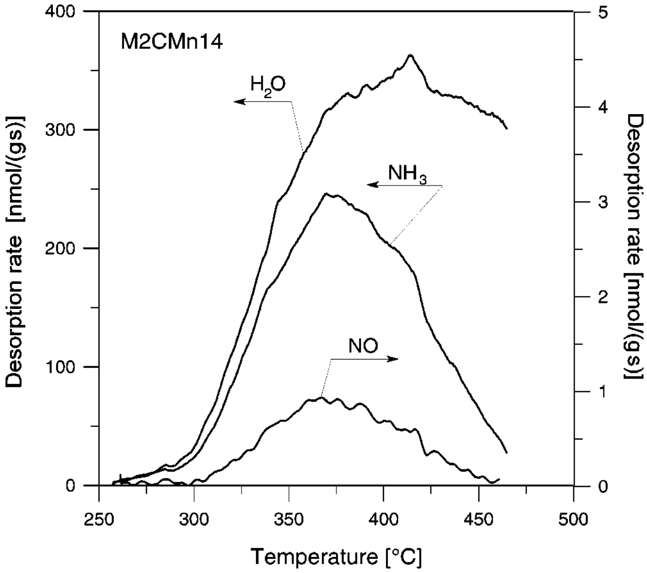

Figure 7. Desorption paterns measured after reaction stopping (stop flow) at 253 °C.

4. Conclusions

(1) The pillared smectites chemisorb NH_3 at 70 °C in amounts 1 μmol/m^2 (below 10% of monolayer) whereas the amounts of chemisorbed NO molecules are about hundred times lower.

(2) The acid-treated pillared smectite modified with carbon and manganese oxide chemisorbs amounts of NO comparable to NH_3. In this case formation of NO_3^- has been confirmed beside the molecular form of weaker adsorbed NO.

(3) Although this sample shows the best catalytic performance, the weaker adsorbed form of NO takes part in the low-temperature SCR of NO_x.

(4) The strongly bound NO_3^- reacts with NH_3 at a temperature higher by about 200 °C.

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