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Selective reduction of NO with NH_3 over pillared clays modified with transition metals

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Abstract

Natural montmorillonite (Wyoming, A-15) was pillared with alumina, titania or zirconia and then modified with copper or iron introduced by the ion-exchange method. The synthesized samples were characterized by XRF (composition), XRD (structure), BET (texture) and tested as catalysts for selective reduction of NO by ammonia. The highest activity in the NO SCR process was found for the TiO_2-intercalated clay doped with copper or iron. The NO and NH_3 chemisorption sites were studied by temperature programmed desorption of NO or NH_3 as well as FT-IR spectroscopy.

Keywords: Pillared montmorillonites; Alumina; Titania; Zirconia; Copper; Iron; NO reduction; NH_3

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1. Introduction

The increase of oil price in 1973 acted as a stimulation for the investigation of new catalytic materials, which could be used to process heavy crude oils [1]. The clays pillared with Al_2O_3, TiO_2 and ZrO_2 were intensively studied as potential catalysts for this process. Although pillared clays (PILCs) were not used as industrial catalysts due to their relatively low hydrothermal stability [2], very intensive studies performed at 1970s resulted in the development of preparation methods of such materials. Possibility of modification of texture parameters, surface acidity, composition, etc., allows preparing clay-based catalysts for specific applications. It is not therefore surprising that modified PILCs have been found to be active, selective and stable catalysts for reduction of NO_x with ammonia and hydrocarbons [3–5].

This paper presents studies of the alumina, zirconia and titania pillared montmorillonites additionally modified with copper or iron as catalysts of NO reduction with ammonia.

2. Experimental

The sodium exchanged Wyoming (A-15) montmorillonite (CEC = 83 meq per 100 g) was used as a raw material for catalysts preparation.

The aluminium hydroxy-oligomeric solution was prepared by a slow addition of 0.1 M NaOH into $AlCl_3$ solution under constant stirring until the molar ratio of OH/Al reached 2.5. The oligomeric solution was aged at the room temperature (RT). In the next step the pillaring solution was added to the suspension containing 1 wt.% of the sodium exchanged montmorillonite (Mt-Na) in deionised water until the Al/clay ratio reached the value of 10 mmol Al/g clay. The mixture was allowed to react at RT for 24 h. Then the modified clay was separated, washed with distillated water until chloride ions were removed, and dried at 120 °C for 12 h.

The Mt-Na clay was pillared with zirconia using an aqueous solution of zirconyl chloride (2.5 mmol Zr/1 g of clay). The pillaring solution was aged at RT. Pillaring of the clay was carried out at 50 °C. The resulting suspension was allowed to react at this temperature for 3 days. Subsequently, the modified clay was separated, washed with distillated water, until chloride ions were removed and dried at 120 °C for 12 h.

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The solution of titanium oligocations was prepared by an addition of $TiCl_4$ into 6.0 M HCl. The mixture was diluted by a slow addition of distillated water to reach the final concentrations of Ti^{4+} and HCl equal to 0.82 and 0.11 M, respectively. The solution was aged at RT. The suitable amount of pillaring agent, required to obtain the Ti/clay ratio of 10 mmol/g of clay, was then added to the vigorously stirred suspension. The montmorillonite was left in contact with the solution for 24 h and then separated by filtration. The product was washed by redispersing it in distillated water, followed by separation. The procedure was repeated until the modified montmorillonite was free of chloride anions. The product was dried at 120 °C for 12 h.

In the next step of catalysts preparation, copper was introduced into the dried pillared clays by the ion-exchange method. About 1 g of the pillared montmorillonite was added to copper nitrate solution (0.02 M). The vigorously stirred suspension of the pillared clays was left in contact with the solution of $Cu(NO_3)_2$ at 60 °C for 12 h. The ion-exchange products were collected by filtration followed by washing with distillated water. The modified montmorillonites were dried at 120 °C for 12 h. Similar procedure was applied for modification of the titania pillared clay with iron.

The chemical composition of the clay samples was determined by X-ray fluorescence method (XRF) using an Oxford 2000 instrument. The structure of the calcined clay samples was studied with a PW3710 Philips X'pert diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å). BET measurements were performed using an ASAP 2010 (Micromeritics). Prior to N_2 adsorption at liquid nitrogen temperature (−196 °C) the calcined clay samples were outgassed at 350 °C under vacuum for 12 h.

The temperature programmed desorptions of NH_3 (NH_3-TPD) or NO (NO-TPD) were carried out in the temperature range of 70–600 °C in a fix bed continuous flow microreactor. The desorption temperature 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 Quartz) connected to the reactor outlet via a heated line. Before TPD experiments the clay sample (50 mg) was outgassed at temperature 400 °C for 1 h in a flow of helium (20 ml/min). Subsequently, the sample was cooled down to 70 °C and saturated for about 30 min in a flow of 1% NH_3/He or 1% NO/He (20 ml/min). Then, the catalyst was purged in a helium flow until a constant baseline level was attained. Desorption was carried out with the linear heating rate ($\beta = 10$ °C/min) in a flow of He (20 ml/min). Calibration of the quadrupole mass spectrometer with commercial mixtures allowed to recalculate the detector signal into a desorption rate.

The pillared montmorillonites pre-adsorbed with NO were studied by FT-IR spectroscopy. The clay sample was outgassed according to the procedure applied in TPD experiments. The outgassed catalyst (400 °C/1 h/He = 20 ml/min) was saturated in a flow of 1% NO/He for 30 min and then purged in a flow of pure helium (20 ml/min) until a constant baseline level was attained. Subsequently, for the sample pre-treated in such a way, FR-IR spectra were recorded using a Bruker IFS 48 spectrometer (1% of a sample in KBr). For comparison measurements for the outgassed samples were also performed.

The modified montmorillonites were studied as catalysts of NO reduction by ammonia. The catalytic tests were performed in a fixed-bed flow reactor system. The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG Quartz) connected on-line to the microreactor. Prior to the reaction, the catalyst (200 mg, particle diameter 125–180 μm) was outgassed in pure helium at 400 °C for 30 min. Composition of the gas mixture used during catalytic runs was $[NO] = [NH_3] = 0.25\%$, $[O_2] = 2.5\%$ at the reactor inlet. Helium was used as a balancing gas at a total flow rate of 40 ml/min. The intensities of the mass lines corresponding to all reactants and products were measured at a given temperature at least for 30 min after the reaction had reached a steady-state.

3. Results and discussion

The chemical composition of the clay materials is presented in Table 1. Apart from components listed in the table also small amounts of MgO, CaO and Na_2O (below 1 wt.%) as well as water were detected in the samples. It should be noticed that the parent clay (Mt-Na) contains large amount of iron. Pillaring of the Mt-Na clay with alumina resulted in an increase of Al_2O_3/SiO_2 ratio from 0.27 to 0.40 wt.%. Dealumination of the montmorillonites, which was observed

Table 1
Composition of catalysts given by XRF

Sample	CuO (wt.%)	Fe_2O_3 (wt.%)	Al_2O_3/SiO_2 (wt.%/wt.%)	TiO_2/SiO_2 (wt.%/wt.%)	ZrO_2/SiO_2 (wt.%/wt.%)
Mt-Na		10.42	0.27	0.01	
Mt-Al		6.72	0.40	0.01	
Mt-Al-Cu	0.47	5.91	0.38	0.01	
Mt-Ti		1.29	0.22	1.83	
Mt-Ti-Cu	0.30	1.24	0.23	2.15	
Mt-Ti-Fe		6.48	0.20	2.37	
Mt-Zr		4.90	0.18	0.01	0.66
Mt-Zr-Cu	0.30	4.89	0.20	0.01	0.63

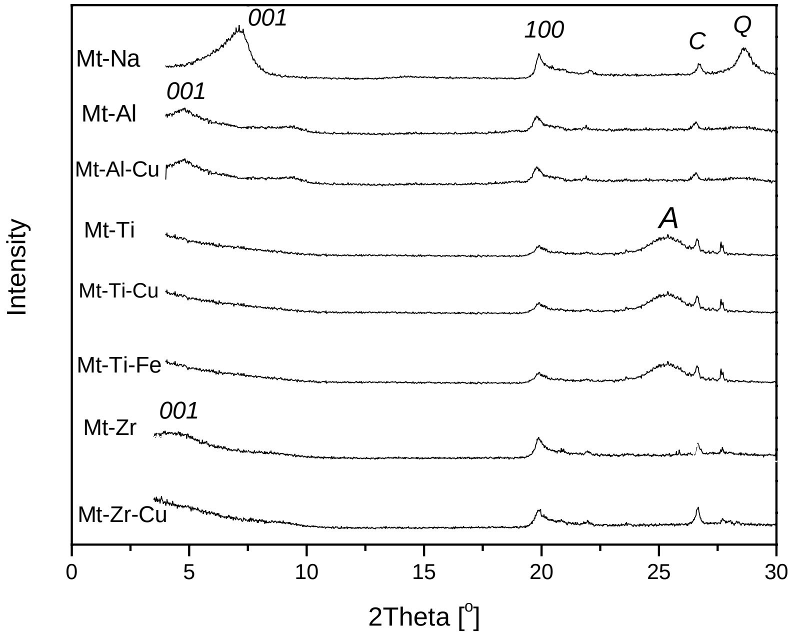

Fig. 1. X-ray diffractograms of pillared montmorillonites.

for the samples intercalated with titania (Mt-Ti) or zirconia (Mt-Zr), is probably caused by extraction of Al^{3+} cations from octahedral positions under the acidic conditions applied during the pillaring process. Amount of copper introduced to the clay samples by the ion-exchange method, did not exceed 0.5 wt.%. Significantly higher amount of iron was introduced into the titania pillared clay. Increase of TiO_2/SiO_2 ratio, which was found after the introduction of transition metals into the Mt-Ti clay, can be explained by a removal of quartz or crystobalite impurities during the ion-exchange process.

The results of structural studies on the pillared montmorillonites are shown in Fig. 1. A shift of (0 0 1) peak in direction of lower values of 2Θ angle, that was observed for the alumina and zirconia modified clays, indicates that metal oxide pillars were successfully introduced into the interlayer space. Estimating the aluminosilicate layer thickness equal to 9.6 Å it was calculated that the interlayer distance increased from 3.2 (Mt-Na) to 9.6 and 11.9 Å for the alumina and zirconia pillared montmorillonites, respectively. In the case of the titania modified clay a lack of (0 0 1) peak was detected. The additional measurements performed in the low 2Θ angle range from 0.4 to 3.0° (not presented in this paper) neither showed the presence of this maximum. These results suggest that in the case of the titania modified clay delaminated structure (non-parallel ordering of clay layers) was obtained. Additional peak detected at $2\Theta = 19.6^\circ$ for the titania intercalated montmorillonite can be attributed to the (1 0 1) reflection of anatase (A). Probably, a part of pillaring agent was deposited on the clay surface and during calcination was decomposed with the formation of separate phase (anatase). Delaminated structure was also found for the zirconia pillared clay modified with copper. The peaks at 26.5 and 28° are attributed to a presence of quartz (Q) and crystobalite (C) impurities in the clay. The results of XRD measurements as well as their detailed description can be found in a previous paper [5].

Table 2 presents BET surface areas (S_{BET}) of the parent clay and its modifications. Pillaring of the Mt-Na clay with alumina, titania and zirconia resulted in an increase of S_{BET} from 38 to 254, 279 and 242 m^2/g, respectively. Introduction of copper to the Al_2O_3- and ZrO_2-pillared clays caused significant decrease of their surface area. It can be explained by a formation of copper oxide clusters, which partially block pores of the pillared clays. Such effect was not observed for the TiO_2-intercalated montmorillonites modified with copper or iron.

The pillared montmorillonites were tested as catalysts of NO reduction with ammonia. N_2 and H_2O are desired products of this process, while N_2O is a side product. Formation of any other gases was not detected. Fig. 2A presents the results of catalytic tests obtained in the presence of the alumina pillared clays. The NO conversion over the Mt-Al catalyst increased from about 100 °C and at temperature 470 °C reaches 75%. Modification of the alumina pillared montmo-

Table 2
Surface area and concentration of chemisorbed ammonia

Sample	S_{BET} (m^2/g)	NH_3 chemisorption (μmol NH_3/g)	NH_3 chemisorption (μmol NH_3/m^2)
Mt-Na	38	37.0	0.97
Mt-Al	254	376.2	1.48
Mt-Al-Cu	138	192.0	1.39
Mt-Ti	279	553.5	1.98
Mt-Ti-Cu	286	460.5	1.61
Mt-Ti-Fe	270	526.5	1.95
Mt-Zr	242	275.9	1.14
Mt-Zr-Cu	198	301.0	1.52

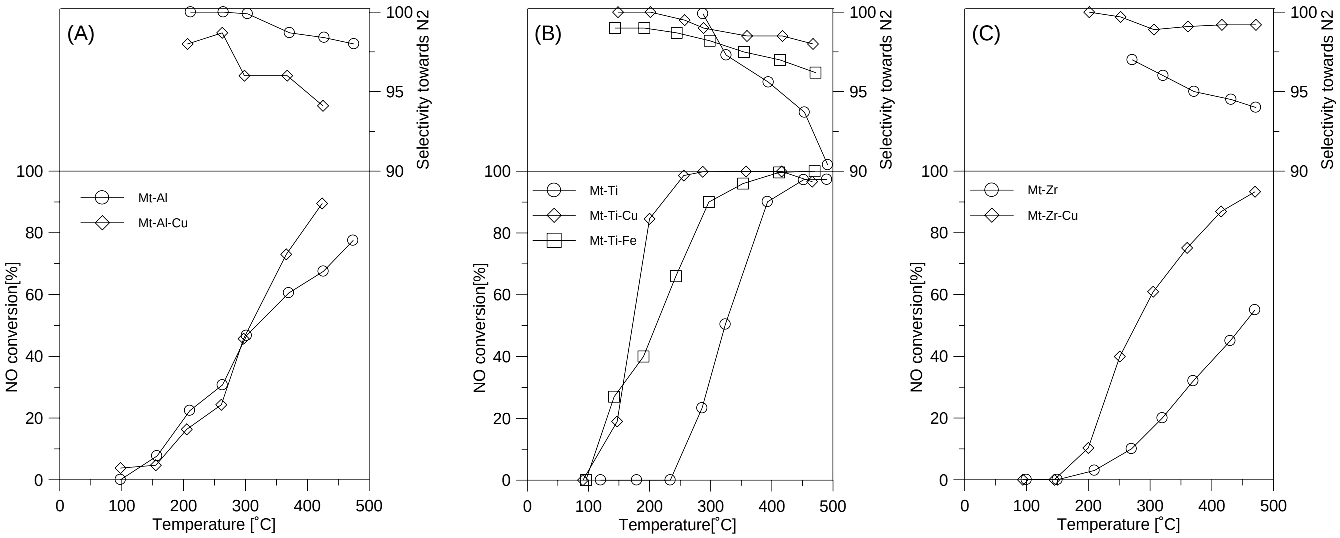

Fig. 2. Results of catalytic tests for alumina (A), titania (B) and zirconia (C) pillared clays.

rillonite with copper significantly increased the reaction rate in the high-temperature region ($T > 300\,^{\circ}\mathrm{C}$) but also decreased selectivity towards nitrogen. Fig. 2B shows the results obtained for the titania pillared montmorillonites. The NO conversion over the Mt-Ti catalyst increased from about 240 °C and reached 96% at temperature 450 °C. The selectivity towards N_2 decreases very sharply with the increase of reaction temperature. The modification of the titania pillared clay with transition metals resulted in a significant increase of its catalytic activity. Reduction NO by ammonia in the presence of TiO_2-intercalated montmorillonites modified with Cu or Fe cations started at temperature as low as 100 °C. At temperature below 150 °C the NO reduction rates over the Mt-Ti-Cu and Mt-Ti-Fe catalysts are very similar, however at higher temperatures conversion of nitric oxide increases faster in the case of the Cu-containing sample. The NO was totally converted in the range of 240–400 °C over Mt-Ti-Cu. At higher temperatures the nitric oxide conversion slightly decreased due to oxidation of NH_3 by oxygen. Such effect was not observed for the Mt-Ti-Fe clay, however the activity of this catalyst was significantly lower than the Mt-Ti-Cu sample. It should be noticed that modification of the TiO_2-pillared clay with transition metals not only drastically increased its catalytic activity but also significantly improved its selectivity to nitrogen.

The results of catalytic tests over the zirconia pillared clays are presented in Fig. 2C. The reduction of nitric oxide in the presence of the Mt-Zr catalyst increased from about 150 °C and reached at 470 °C about 55%. Copper introduced into the Mt-Zr clay increased its catalytic activity and selectivity to N_2. NO reduction by ammonia started at about 150 °C and at temperature 470 °C increased to 93%.

The interaction of NH_3 and NO molecules with the catalysts surface was studied by temperature programmed desorption (TPD) methods. Fig. 3 shows the ammonia desorption patterns obtained for the studied samples, while surface concentrations of chemisorbed ammonia are compared in Table 2. Basic NH_3 molecules are chemisorbed on the acidic surface sites, so values listed in the table represent surface acidity of the clay samples. The NH_3 desorption spectrum obtained for the Mt-Al montmorillonite is spread in the range of 130–500 °C and consist of at least two unresolved maxima centered at 170 and 280 °C, respectively. The low-temperature peak can be assigned to NH_3 desorption from weak acidic Brønsted sites localized on the montmorillonite layers, while high-temperature maximum is related to ammonia desorption from acidic centers present on the metal oxide pillars [6]. Modification of the alumina pillared clay with small amount of copper slightly decreased intensity of high-temperature desorption peak.

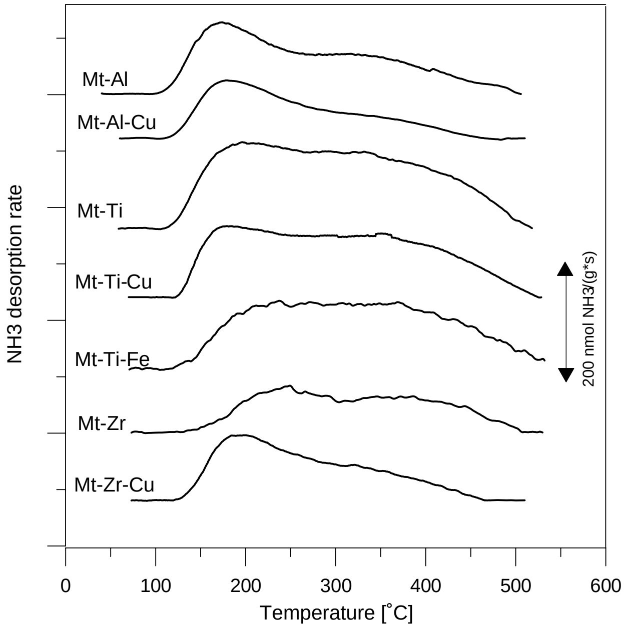

Fig. 3. Ammonia desorption patterns obtained for modified clay materials.

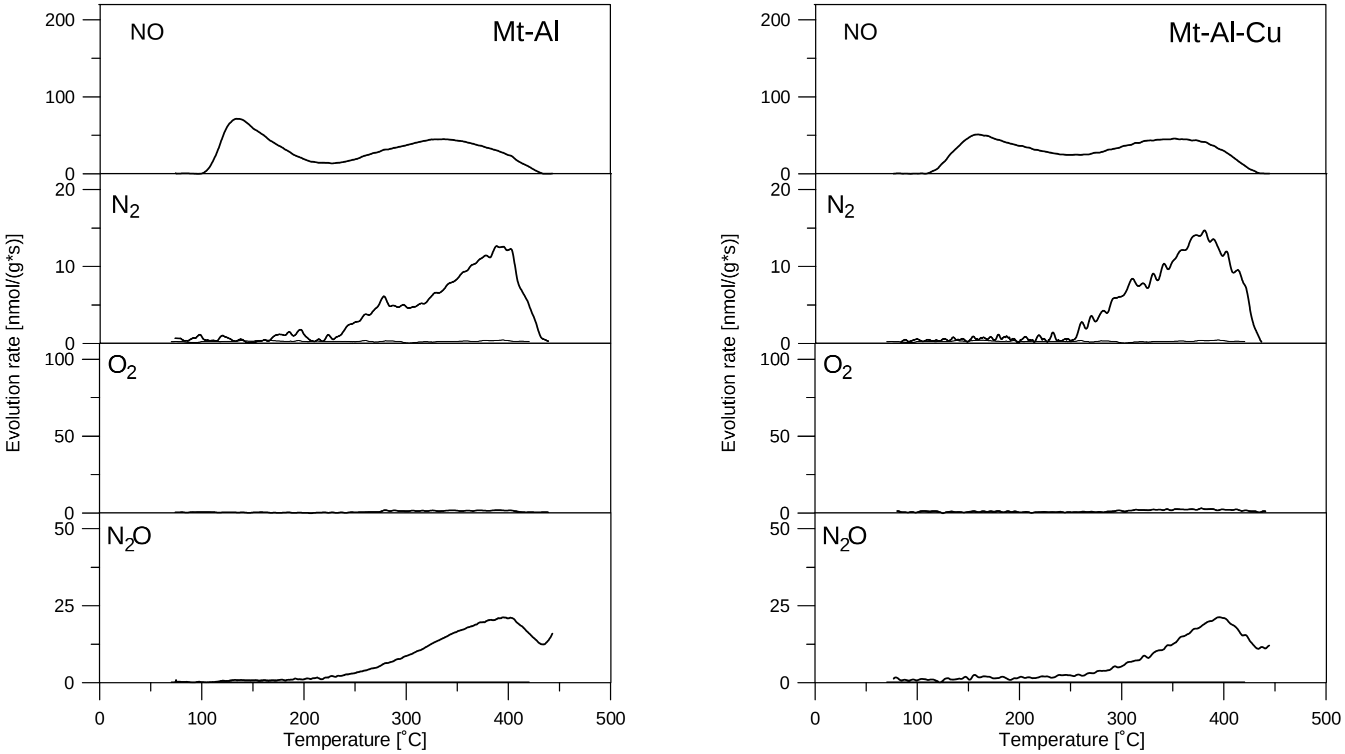

Fig. 4. Results of NO-TPD measurements for alumina pillared montmorillonites.

The NH_3-TPD spectrum recorded for the titania pillared clay consists of at least two unresolved maxima centered at about 200 and 350 °C. The surface acidity of the Mt-Ti sample is significantly higher than that measured for the Mt-Al clay mainly due to larger concentration of stronger acid centers. Modification of the Mt-Ti sample with copper only slightly decreased intensity of desorption pattern, while for the Fe-containing clay (Mt-Ti-Fe) a shift of the low-temperature maximum in direction of higher temperatures occurred.

Desorption of ammonia from the Mt-Zr sample took place in the temperature range of 130–510 °C. The NH_3-TPD pattern consists of two unresolved maxima centered at about 240 and 380 °C. Introduction of transition metals into the zirconia pillared clay resulted in a shift of the low-temperature maximum in direction of lower temperatures and a decrease in intensity of the high-temperature peak.

The results of NO-TPD experiments are shown in Figs. 4–6. Apart from desorption of nitric oxide also emission of N_2, O_2 and N_2O was detected. Fig. 4 presents the

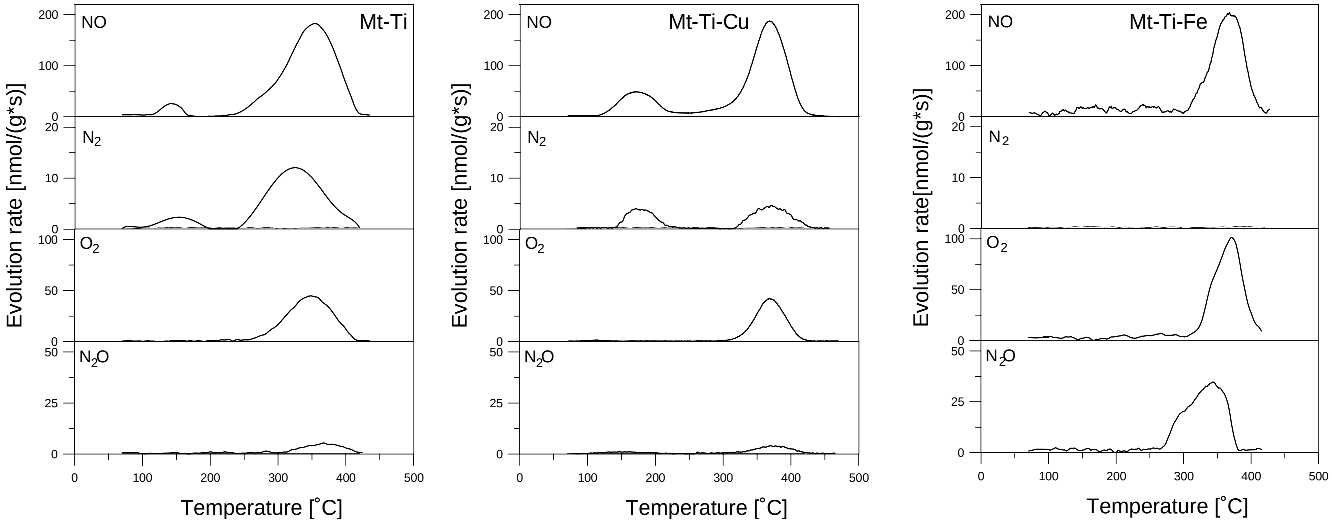

Fig. 5. Results of NO-TPD measurements for titania pillared montmorillonites.

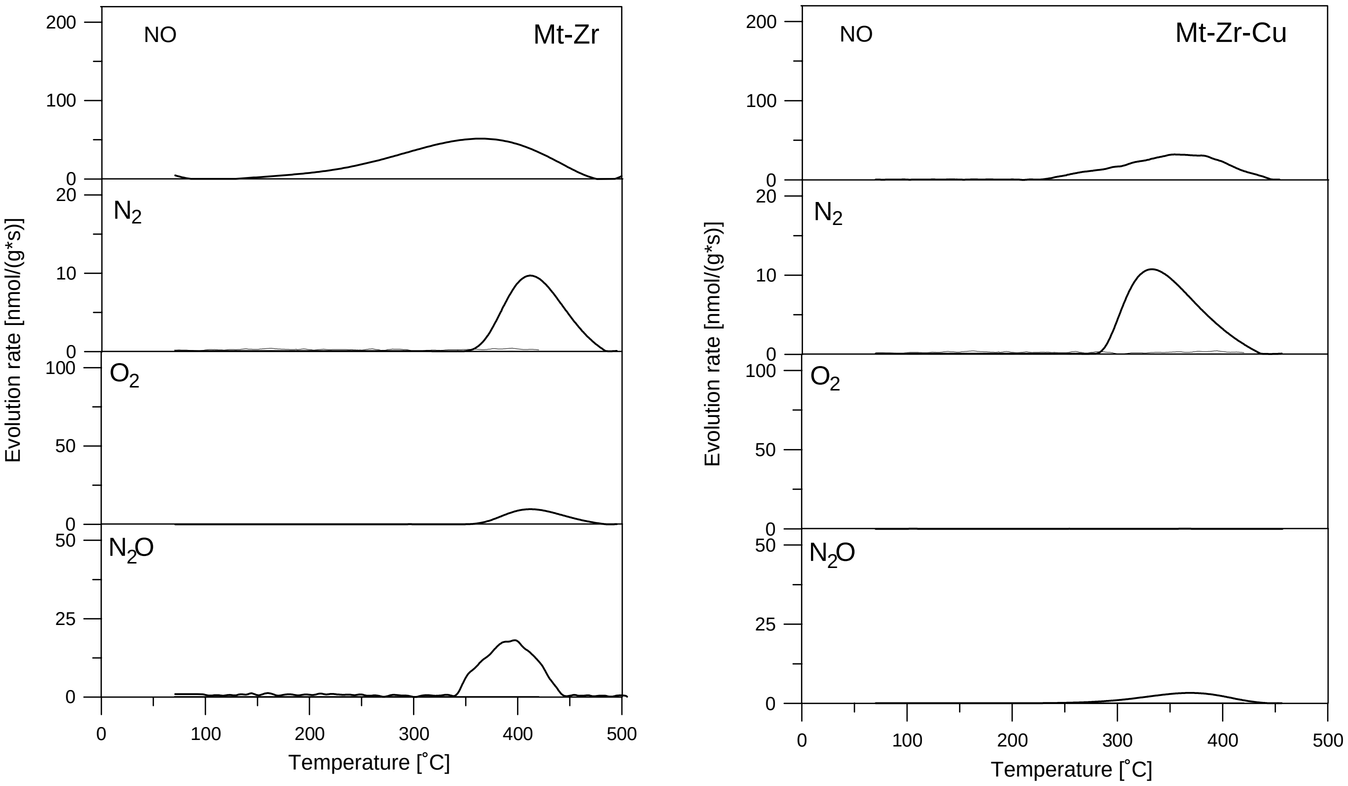

Fig. 6. Results of NO-TPD measurements for zirconia pillared montmorillonites.

results obtained for the alumina pillared clays. The NO desorption pattern recorded for the Mt-Al sample is spread in the range of 100–430 °C and consists of two maxima centered at about 140 and 340 °C. Modification of the alumina pillared clay with copper practically did not influence the NO desorption patterns. In order to identify the nature of these surface species the FT-IR spectra were recorded for the clay samples pre-adsorbed with NO. For comparison the spectroscopic measurements for the outgassed montmorillonites were performed. The examples of obtained FT-IR spectra are presented in Fig. 7. For all the NO pre-treated samples an additional peak at about 1385 cm^{-1}, which is attributed to the presence of free NO_3^- anions [7], appeared.

Fig. 5 shows the results of NO-TPD measurements performed for the titania pillared montmorillonites. The NO desorption pattern obtained for the Mt-Ti sample consists of two maxima. The first small peak is centered at 140 °C, while the second one, much more intensive, at about 350 °C. Part of weakly chemisorbed NO is decomposed to nitrogen and oxygen, however only N_2 evolution was detected at temperature below 200 °C. Thus, oxygen was bounded to the sample or oxidized stronger chemisorbed NO molecules. The high-temperature peaks of NO, N_2, O_2

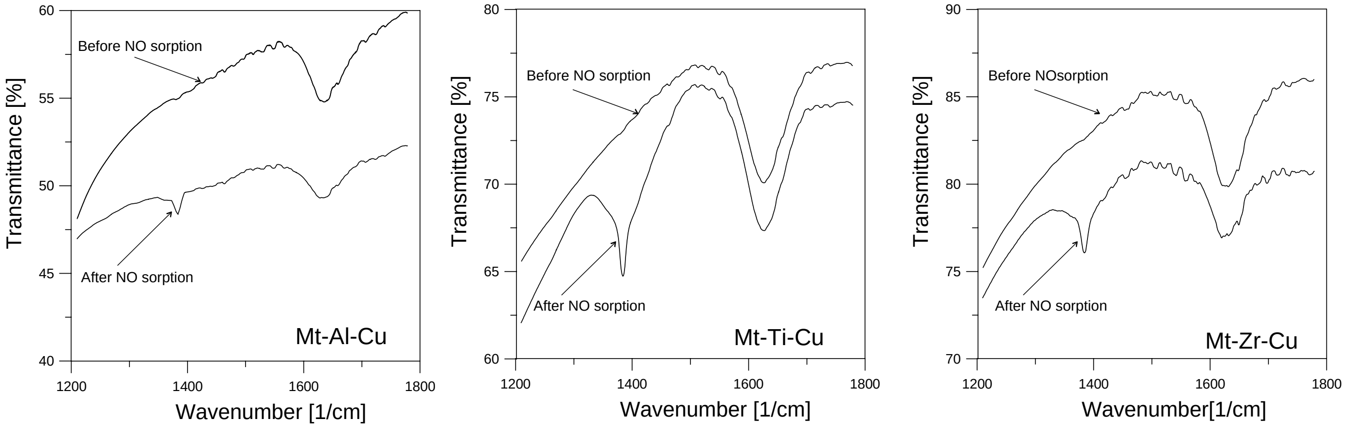

Fig. 7. FT-IR spectra obtained for the samples before and after pre-treatment with NO.

and N_2O evolutions are caused by thermal decomposition of surface nitrates, which were formed during nitric oxide chemisorption and/or by oxidation of surface NO species by oxygen formed from decomposition of nitric oxide at lower temperatures ($T > 200\,^{\circ}C$). Very similar results were obtained for the Mt-Ti-Cu sample, however in this case a significant increase in intensity of low-temperature NO desorption maximum and a decrease in amount of nitrogen, emitted in the range of 300–450 °C, were observed. Modification of the titania pillared montmorillonite with iron resulted in disappearance of low-temperature NO desorption peak and increase in O_2 and N_2O evolution at higher temperatures ($T > 270\,^{\circ}C$). Emission of nitrogen was not observed in the whole studied temperature range.

The results obtained for the zirconia pillared clays (Fig. 6) significantly differ from those recorded for the alumina or titania intercalated montmorillonites. In the case of the Mt-Zr sample NO desorption took place in the temperature range of 140–460 °C with maximum at about 370 °C. At higher temperatures ($T > 330\,^{\circ}C$) evolution of gas products of surface nitrates decomposition (NO, N_2, O_2 and N_2O) was detected. Modification of the zirconia pillared clay with copper resulted in decrease of NO and N_2O emissions and lack of O_2 evolution.

4. Conclusions

Pillaring of the parent montmorillonite with Al_2O_3 or ZrO_2 resulted in increase of the interlayer distance from 3.2 to 9.6 and 11.9 Å, respectively, while the clay intercalated with TiO_2 was characterized by the delaminated structure. The surface area of the parent montmorillonite ($38\,m^2/g$) increased by above $200\,m^2/g$ after pillaring with metal oxides.

The catalytic performance of the clay samples in reduction of NO by ammonia strongly depended on the kind of introduced metal oxide pillars and transition metal. Among the studied catalysts the highest activity was measured for the titania pillared montmorillonites modified with copper. However, for this sample the decrease of NO conversion due to ammonia oxidation was observed at higher temperatures ($T > 400\,^{\circ}C$). The TiO_2-pillared clay modified with iron was found to be less active than Mt-Ti-Cu catalyst, however its activity was significantly higher than the ZrO_2 and Al_2O_3 intercalated montmorillonites. Introduction of transition metals into the zirconia or titania pillared clays significantly increased their selectivity towards nitrogen. Opposite effect was observed for the Al_2O_3 intercalated clays.

Pillaring of the parent clay with metal oxides increased surface concentration of chemisorbed ammonia due to opening of the interlayer space and supplying new acidic sites localized on the pillars surface. Modification of the alumina or titania intercalated montmorillonites with transition metals decreased surface acidity. Opposite effect was observed for the zirconia pillared clay, which after the introduction of copper exhibited increase in chemisorbed ammonia concentration.

Two types of NO adsorption sites were found for the alumina and titania pillared montmorillonites. In the case of the zirconia intercalated clay the only one NO desorption peak, related to relatively strong chemisorbed nitric oxide, was detected. The presence of surface nitrates, that decompose with the evolution of NO, N_2, O_2 and N_2O, was proved for the studied clay catalysts.

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