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Ammonia and water sorption properties of the mineral-layered nanomaterials used as the catalysts for NO_x removal from exhaust gases

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Abstract

The object of the study is the influence of acidity and hydrophilic properties of the surface of catalyst of the selective catalytic reduction (SCR) of nitrogen oxides by NH_3. A series of catalysts prepared with the ZrO_2-pillared montmorillonite from Jelsovy Potok have been promoted with manganese oxides. A part of the Na^+-montmorillonite form has provisionally been treated with the 20% HCl.

The acidity of materials was studied by the ammonia adsorption method at the temperature of 273 and 373 K. Acidic properties of catalysts depend on the step of the support preparation—the acidic activation. The activity of the SCR reaction of acid untreated support and the catalyst with MnO_x which had few stronger acid centres was lower than the activity of the acid pre-treated catalyst. In this case the support had more strong acid centres. The active material of MnO_x increased the NO conversion but not the influence on the amount of ammonia sorption. These centres are probably not acidic centers. The hydrophilic properties were studied by water vapour sorption at the temperature of 298 K. All the samples adsorbed the same amount of water, which suggests that the NO conversion does not influence hydrophilic properties. Water molecules were physically sorbed on the surface of materials and they were replaced with NH_3 in the presence of ammonia.

Keywords: Montmorillonite; Water sorption; Ammonia sorption; SCR of NO by NH_3

1. Introduction

The research of catalysts for the sake of the removal of volatile pollutions such as NO_x is conducted with a view to protect the environment. Three major catalysts of the with selective catalytic reduction of nitrogen oxides with ammonia (SCR by NH_3) are effective in different temperature ranges: the Pt-type catalyst in a low temperature range of 423–573 K, the V_2O_5/TiO_2 catalyst in a medium temperature range of 533–698 K and zeolite in a higher temperature range (624–869 K). For commercial installations V_2O_5/TiO_2 are used either as extruded monoliths or as deposited ones on a number of installations that use a zeolite technology [1].

Currently other materials are studied, which are very interesting due to their possibilities of modification. Among those materials the mineral-layered nanomaterials can be found which have the best catalytic properties at a higher temperature range [2–4]. An element of montmorillonite modification can be: the intercalation with different cations, an acidic treatment of starting materials with such acids as HCl or H_2SO_4 and the introduction of carbon deposits.

The catalytic properties of montmorillonites may be improved by the introduction of an active material on the support surface. Bosch and Janssen's review shows catalysts of the selective catalytic reduction based on modified montmorillonites promoted with oxides and hydroxides of V^{5+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, $Mn^{2+/3+}$, Ni^{2+} and Co^{2+} [5]. The activity of catalysts increases in the presence of these active materials. One of examples may be a montmorillonite modified by Al_2O_3- or a TiO_2-pillared clay with Cu or Co studied by Chmielarz et al. [6]. The best catalyst was the Al_2O_3-pillared clay promoted with 18% Co which had 90% NO conversion at the temperature of 750 K. The activity of the SCR for catalysts based on the TiO_2-pillared montmorillonite was not influenced by the Co amount and all the samples had ca. 100% NO conversion and ca. 98% selectivity to N_2 in the temperature range of 673–773 K. Similar effects were shown for the TiO_2-pillared montmorillonite promoted with Cu in the temperature range of

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573–723 K. Long and Yang [7] have studied the effect of Ce promoted with the Fe^{3+} TiO_2-pillared clay in the SCR reaction in the temperature range of 573–723 K. The NO conversion increased drastically in this temperature zone of between 45 and 90%. The selectivity of N_2 was 100% at the temperature of 573–673 K, but it decreased to 99.4% at 723 K.

The main reactions of selective catalytic reduction of nitrogen oxides are:

$$6NO + 4NH_3 \Leftrightarrow 5N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \Leftrightarrow 7N_2 + 12H_2O$$

$$4NO + 4NH_3 + O_2 \Leftrightarrow 4N_2 + 6H_2O$$

These are the reactions between nitrogen oxides from exhaust gases and ammonia molecules which are bonded on the active centres of the catalyst surface. The number of these centres is very important. One of the types of these centres may be the Lewis and Brønsted acidic centre. Therefore, acidic properties of the catalyst and the support surface as one of the elements characteristic of the modified montmorillonite influenced the catalytic activity of the SCR reaction. The acidity of catalysts may be modified by means of different methods of preparation, such as a kind of an exchange of cations and the starting material. Each step of the preparation leads to differences between the amount and the type of the acid sites: Lewis and Brønsted [8–10]. The acidity of surface may be studied by different methods. One way is the sorption of ammonia [11]. Ammonia molecules bond with montmorillonites through the dispersing interaction (physical sorption) and the electrostatic interaction. The NH_3 molecules may be coordinated by interlayer cations or react with water molecules forming the NH_4^+ ions and metal hydroxides. The NH_4^+ ions may be bonded with gaseous ammonia by hydrogen bonds. The number of the electrostatic interaction bonding the NH_3 molecules may be determined on the basis of the irreversibility of ammonia sorption. The amount of the sorbed ammonia depends on the temperature, the exchanged cations and the pressure. In a relatively low pressure ammonia molecules are adsorbed on the outside surface of the montmorillonite, however, an increase of the pressure causes penetration into interlayer spaces when ammonia molecules are directly bonded with the exchanged ions they probably form three-dimensional aminocation complexes.

The presence of water in the reaction mixture and the interaction between water molecules and the catalyst surface may also play an important role with regard to the catalytic properties [12–14]. For example, the surface acidity of the TiO_2-pillared montmorillonite as shown by Long and Yang [7] influenced the SCR reaction. The authors tested the 5.93% Fe on the TiO_2-pillared montmorillonite after the contact with the 5% H_2O in helium for 15 min at 673 K and cooled it to the room temperature in the presence of water. In the presence of water ammonia formed coordinated NH_3 and/or formed NH_4^+ ions with surface hydroxyl groups. The comparison with the sample cooled to the room temperature in helium showed that the NH_4^+ band on the first sample was slightly stronger, which suggested that the ammonia adsorption on the Fe-TiO_2-pillared montmorillonite surface did not inhibit the SCR reaction. In the absence of ammonia water molecules could be adsorbed on the catalyst surface. However, the adsorbed H_2O molecules were displaced by ammonia presented in the reaction conditions. This suggests that the basicity of ammonia is stronger than that basicity of water. However, when studying the effect of water vapour on the stability of MnO_x on the ZrO_2-pillared montmorillonite Chmielarz et al. [15] introduced carbon deposits as SCR by the NH_3 catalyst and observed that in the presence of water the activity of the obtained catalyst decreased, although only by a few percent (from ca. 95 to 90%).

The objective of this work was to prepare a series of catalysts prepared with the ZrO_2-pillared montmorillonite from Jelsovy Potok promoted with manganese oxides. A part of the Na^+-montmorillonite form was provisionally treated with the 20% HCl. The aim was to study the influence of acidity of supports and the catalysts surface on the activity of the selective catalytic reduction (SCR) of nitrogen oxides by NH_3 and to answer a question as to how the type and the number of the acid centres changed after the acid treatment of the support and after having been doped with the MnO_x active material. The author also analysed the relation between hydrophilic properties and the catalytic activity of the prepared materials.

2. Experimental

2.1. The preparation of catalysts

The starting material was the montmorillonite from Jelesovy Potok. The composition of this material (%) as given by the X-ray fluorescence method XRF is: N_2O 2.48, MgO 3.23, Al_2O_3 18.90, SiO_2 58.69, P_2O_5 0.05, K_2O 0.36, CaO 0.07, TiO_2 0.20, MnO 0.08 and Fe_2O_3 3.54 [16].

The 1% suspension of the montmorillonite was conducted with 1 M NaCl to the Na^+-montmorillonite form. Clay were separated by filtration and washed with distilled water until Cl^- free ($AgNO_3$ test). A part of the Na^+-montmorillonite was activated with 6 M HCl (20 cm^3/g of clay) at the temperature of 369 K for 4 h and washed with distilled water until the pH value of the resulting washed solution was 7. Further, the Na^+-montmorillonite and the acid activated montmorillonite were dissolved slowly in the pillaring solution and stirred at 373 K for 1 day. The concentration of the pillaring solution was 0.1 M $ZrOCl_2$, the ratio of OH:Zr of 1 and 10 mmol Zr^{4+}/g montmorillonite. All the samples were calcined for 5 h at the temperature of 723 K.

The active material was supported by the water solution of 0.1 M $Mn(NO_3)_2$ with or without saccharose. The weight ratio of Mn^{2+}:saccharose for the group acid activated ZrO_2-montmorillonite was 9, 20 or 50.

Table 1 shows each step of the preparation, the names of all the samples, and additionally, the summarized parameters of the texture: the specific surface area S_{BET}, the volume of micro- and mesopores and the structure—d_{001} distance based on the data published by Grzybek et al. [16]. The exact characterisation of the texture (by using low temperature argon sorption)

Table 1
Preparation, names of studied samples, parameters of texture based on the data published in Ref. [16]: the specific surface area S_{BET}, the volume of micro- and mesopores and the structure—d_{001} distance

Support	Intercalation with Zr^{4+}[a]	Active material of Mn^{2+} (%)	Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	d_{001} (nm)
A[b]	+	–	A-Zr	300	0.15	0.03	1.96
	+	0.6[c]	A-ZrMnS9	313	0.12	0.03	1.96
AH[d]	+	–	AH-Zr	306	0.10	0.08	1.96
	+	1.8[e]	AH-ZrMn	223	0.06	0.17	1.96
	+	1.9[c]	AH-ZrMnS9	222	0.07	0.17	1.96
	+	1.8[f]	AH-ZrMnS20	232	0.06	0.17	1.96
	+	1.8[g]	AH-ZrMnS50	224	0.06	0.17	1.96

n.m.: not measured.

[a] Intercalation with 10 mmol Zr^{4+}/g mont., OH:Zr = 1.

[b] Na^+-montmorillonite untreated with HCl.

[c] Introduction of MnO_x from 0.1 M $Mn(NO_3)_2$ water solution with saccharose, Mn:Sach weight ratio 9.

[d] Na^+-montmorillonite treated with 20% HCl for 4 h at 369 K.

[e] Introduction of MnO_x from 0.1 M $Mn(NO_3)_2$ water solution without saccharose.

[f] Introduction of MnO_x from 0.1 M $Mn(NO_3)_2$ water solution with saccharose, Mn:Sach weight ratio 20.

[g] Introduction of MnO_x from 0.1 M $Mn(NO_3)_2$ water solution with saccharose, Mn:Sach weight ratio 50.

and the structure (by using the X-ray diffraction; XRD method) and the study of the distribution of active material on the samples surface (based on the photoelectron spectroscopy XPS method) were discussed in previous papers [16–18].

2.2. The method of the acidity and hydrophilic study

Acidity was studied by the following method: the ammonia sorption (physical and chemical) was carried out at 273 K by means of the measurement of the first isotherm at 273 K, followed by outgassing at the same temperature and subsequently the second isotherm again at 273 K and another outgassing at 373 K, and finally the third isotherm again at 273 K. Thus, the first isotherm represents the sum total of physical and chemical adsorption, the second isotherm is connected only with the physical adsorption, and the difference between the first and the second isotherm is the total chemisorbed amount (the total acidity). The third isotherm is connected with the physical and the strong chemical adsorption, and in fact the difference between the third and the second isotherm presents the number of the physical acid sites and the stronger acid sites, therefore the degree of strong acidity may be calculated. The amount of the adsorbed ammonia and surface concentration of NH_3 was calculated by the absolute pressure of 0.07.

Additionally, the acidity of samples A-Zr, AH-Zr and A-ZrMnS9 was compared with the data published by Chmielarz et al. [19]. The authors used the temperature programmed desorption of ammonia (the TPD method) after the NH_3 adsorption at 343 K.

The hydrophilic properties of water vapour sorption at 298 K were measured with a standard volumetric equipment.

2.3. Catalytic performance [16]

The data of the selective catalytic reduction of NO with ammonia were published by Grzybek et al. [16]. The SCR reaction was studied in a fixed-bed reactor under the following conditions: the reaction mixture, 800 ppm NO, 800 ppm NH_3 and 3% O_2 in helium; the mass of catalyst 0.4 g; before the reaction the samples were heated for 2 h at 573 K in helium (the flow rate of 100 cm^3/min) in order to decompose the rest of nitrate which could be left on the surface after impregnation; the analysis of the educts/products (NO, N_2O) was carried out by a NDIR analyzer.

3. Results and discussion

Catalytic properties are summarized in Table 2 based on the data published by Grzybek et al. [16]. Table 2 shows that the maximum NO conversion was at the temperature of 653 K. The ZrO_2-pillared support treated with HCl and untreated demonstrated a low activity (12 and 16% NO conversion, respectively). Merely a 5% increase of the NO conversion was studied after the promotion of the A-Zr support with the active material of MnO_x. However, the introduction of manganese oxides acid treated support causes the increase of the NO conversion from 12 to 61–90% depending on the method of the MnO_x introduction. For the best AH-ZrMnS50 catalyst the NO conversion was 90%. In Table 2 there is purposefully no selectivity to N_2 because all the obtained

Table 2
The selective catalytic reduction of NO with ammonia has been studied in a fixed-bed reactor under the following conditions: the reaction mixture, 800 ppm NO, 800 ppm NH_3 and 3% O_2 in helium; the mass of catalyst 0.4 g at the temperature range of 493–693 K (the basic data published in Ref. [16])

Sample	NO conversion (%)					
	493 K	533 K	573 K	613 K	653 K	693 K
A-Zr	4	5	7	10	16	23
A-ZrMnS9	12	13	15	17	21	25
AH-Zr	5	4	6	9	12	17
AH-ZrMn	30	48	65	76	80	76
AH-ZrMnS50	37	62	77	87	90	88
AH-ZrMnS20	20	30	48	59	69	73
AH-ZrMnS9	19	28	41	53	61	65

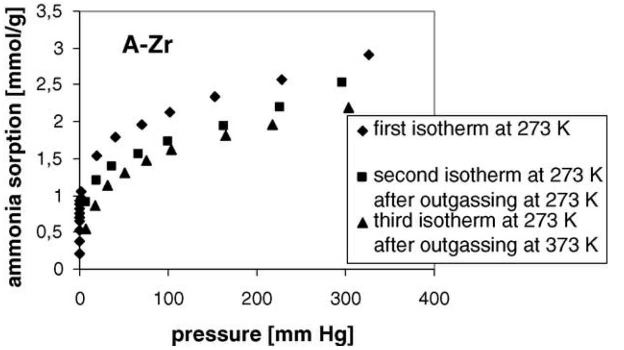

Fig. 1. Ammonia adsorption (mmol/g) for the A-Zr support measured three times consecutively: the first isotherm at 273 K after a preliminary outgassing, the second isotherm at 273 K after outgassing at 273 K and the third isotherm at 273 K after outgassing at 373 K. The first isotherm measured on a fresh sample, the second and third on the sample of ammonia sorbed in advance.

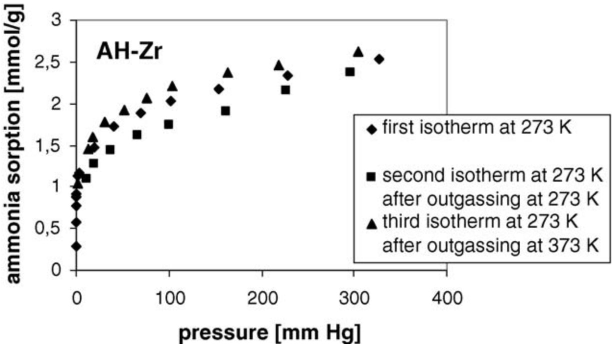

Fig. 3. Ammonia adsorption (mmol/g) for the AH-Zr support measured three times consecutively: the first isotherm at 273 K after a preliminary outgassing, the second isotherm at 273 K after outgassing at 273 K and the third isotherm at 273 K after outgassing at 373 K. The first isotherm measured on a fresh sample, the second and third on the sample of ammonia sorbed in advance.

materials have the common feature: the selectivity to N_2 is practically 100% (within the experimental error).

It may be asked what the correlation is between the acidity after an acidic modification and the activity of support and catalyst? It may be asked whether the MnO_x active material changes the acidity of the catalyst surface?

The acidity study is presented below. Figs. 1–4 show three subsequently measured isotherms of ammonia for samples A-Zr, A-ZrMnS9, AH-Zr and AH-ZrMnS9, respectively. All the isotherms have a similar curve and belong to the first type of the IUPAC classification. This suggests a monolayer coverage of supports and catalysts surface by ammonia molecules. In the absolute pressure range of $0.015 < p/p_0 < 0.12$ the isotherms are parallelly connected.

In Table 3 the amount of chemisorbed ammonia and surface concentration may be seen and also the coverage of the surface by the ammonia monolayer calculated on the assumption that the ammonia molecules cover the surface of 15×10^{-19} m^2 [20].

The ammonia sorption on the A-Zr, AH-Zr supports and A-ZrMnS9 and AH-ZrMnS9 catalysts was studied at two temperatures: 273 and 373 K. A similar study has been carried out by Flego et al. [21]. The authors studied the formation of the NH_4^+ cations after the reaction of ammonia with Al_2O_3-pillared montmorillonite (using the FT-IR spectroscopy method) at three initial pressures of ammonia (10, 50 and 100 mbar) and for the pressure range of 100 mbar—at the room temperature and the temperature of 373, 473 and 573 K. The physical sorption was removed at the room temperature. The small number of Lewis acid sites was due to the presence of Na^+ cations and Al^{3+}-Lewis acid sites.

Table 3 shows that at the temperature of 273 K the amount of chemisorbed ammonia for the A-Zr support was 371 μmol/g and the NH_3 surface concentration 1.2 μmol/m^2, respectively. In Fig. 1 it may be observed that difference between the first and the second isotherm is bigger than between the second and the third assuming that the weak acidic centres are more numerous than the strong ones.

The amount of ammonia chemisorption for the AH-Zr support and its surface concentration at 273 and 343 K shows a drastic difference. The NH_3 sorbed amount and concentration of NH_3 on the surface at 273 K increases from 172 μmol/g and 0.6 μmol/m^2 to 339 μmol/g and 1.1 μmol/m^2 at 343 K, respectively. It is possible that in a higher temperature

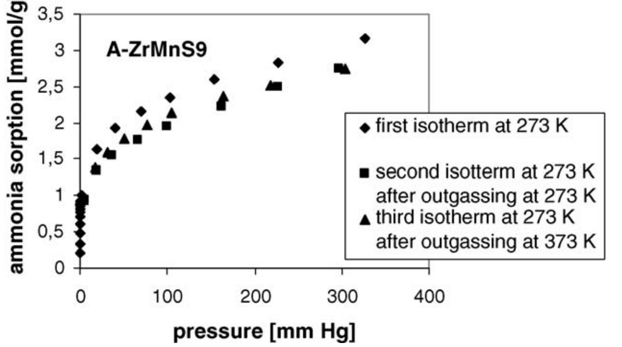

Fig. 2. Ammonia adsorption (mmol/g) for the A-ZrMnS9 catalyst measured three times consecutively: the first isotherm at 273 K after a preliminary outgassing, the second isotherm at 273 K after outgassing at 273 K and the third isotherm at 273 K after outgassing at 373 K. The first isotherm measured on a fresh sample, the second and third on the sample of ammonia sorbed in advance.

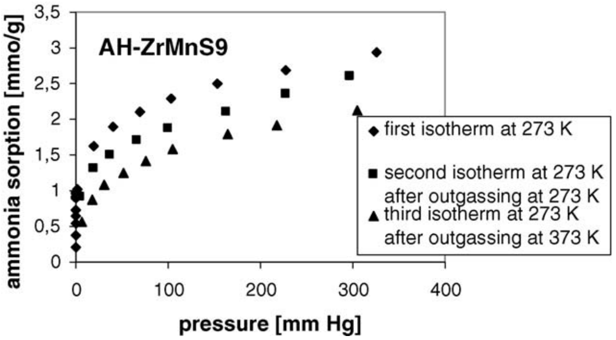

Fig. 4. Ammonia adsorption (mmol/g) for the AH-ZrMnS9 catalyst measured three times consecutively: the first isotherm at 273 K after a preliminary outgassing, the second isotherm at 273 K after outgassing at 273 K and the third isotherm at 273 K after outgassing at 373 K. The first isotherm measured on a fresh sample, the second and third on the sample of ammonia sorbed in advance.

Table 3
Parameters of a specific surface and acidity of the studied samples

Sample	Temperature of chemisorption (K)	Amount of chemisorbed NH_3 (μmol/g)	NH_3 surface concentration (μmol/m^2)	Coverage of surface by NH_3 monolayer[a]
A-Zr	273	371	1.2	11.2
AH-Zr	273	172	0.6	5.1
A-ZrMnS9	273	345	1.1	9.9
AH-ZrMnS9	273	337	1.5	13.7
A-Zr[b]	343	222	0.7	6.3
AH-Zr[b]	343	339	1.1	9.9
A-ZrMnS9[b]	343	200	0.6	5.4

[a] The amount of sorbed NH_3 (μmol/g), the NH_3 surface concentration (μmol/m^2) and the coverage of the surface by the NH_3 monolayer published in Ref. [20].
[b] Basic information on the ammonia molecule published in Ref. [19].

ammonia molecules react with samples of the surface, in addition forming new acid sites. The second isotherm is situated below the first isotherm but the third isotherm is situated above the first and the second one (Fig. 3). This also suggests a change of the acidity of the surface through the formation of new acid sites. In this case the calculation of the number of the acid sites on the ‘‘fresh’’ catalyst and the ‘‘after sorption’’ catalyst as well as the comparison of this value is impossible but it only demonstrates that the surface has been changed.

The comparison of the ammonia chemisorbed amount of the A-Zr and AH-Zr supports at 273 K shows a decrease of the NH_3 sorption by about 50%, that suggests the acidic activation leads to the decrease of the number of weak acidic centres. However, Figs. 1 and 3 show that at temperature 373 K the acid treated support may be enriched by strong acid centres. A similar effect was observed by Grzybek et al. [11] who studied the ammonia sorption on the Al_2O_3-pillared montmorillonite with the introduced carbon deposits additionally activated with HCl. The long time (90 min) of the acid pre-treatment and the intercalation with Al^{3+} hydroxycations caused an increase in the number of the acid sites.

To summarize, the use of a suitable element of the support preparation such as the acid treatment may control the acidity of materials.

The amount of the chemisorbed ammonia at 273 and 343 K for catalyst A-ZrMnS9 is 345 and 200 μmol/g, respectively, and the NH_3 surface concentration is 1.1 and 0.6 μmol/m^2, respectively (Table 3). It follows that 42% of the acid sites are stronger than the other. The comparison of the ammonia sorption isotherms for A-ZrMnS9 (Fig. 2) shows that the second and third isotherms of acid untreated catalysts practically agree (within the experimental error), thus the weak acid centres are predominant. In conclusion: the A-Zr support and the A-ZrMnS9 catalyst decrease the ammonia sorption by about 7% at 273 K and 10% at 343 K, and also decrease the coverage of the surface by the ammonia monolayer from 11.2 and 6.3% (at 273 K) to 9.9 and 5.4%, respectively. On the other hand, Table 2 demonstrates an insignificant increase of the NO conversion from 16 to 21% at 653 K. This suggests that the weak acidic centres respond to small catalytic effect in the reaction studied, but manganese oxides are not strong acidic centres.

However, in the case of the AH-ZrMnS9 catalyst the NH_3 chemisorbed amount and the concentration of NH_3 on the surface at 273 K are 337 μmol/g and 1.5 μmol/m^2, respectively. Unfortunately, the sorption at 343 K was not measured, but Fig. 4 makes it possible to calculate (at the temperature of 373 K, not 343 K) the value of the NH_3 chemisorption, which is 90 μmol/g and 0.4 μmol/m^2. The coverage of the surface by NH_3 molecules is bigger than in other samples (13.7% at 273 K). The chemisorption of the ammonia molecules on the support is less than on the catalyst (at 273 K).

The comparison of catalysts shows that the NO conversion with the AH-ZrMnS9 catalyst is three times larger than with the A-ZrMnS9 catalyst (Table 2). This suggests that strong acid centers of acid treated support respond to a higher SCR activity.

To summarize, the catalytic active centers formed as a result of the introduction of small clusters of manganese oxides to the support surface are not typical ammonia sorption centers. However, the acidity of the surface is determined by a preliminary acidic activation. The literature discusses the influence of different active materials on the surface acidity. For example, Long and Yang [7] have studied the Fe-exchanged TiO_2-pillared montmorillonite with a different amount of Fe. The ammonia adsorption was preformed at the room temperature in the flow of 1% NH_3 in helium for 30 min. All the samples with Fe had more Brønsted acid sites than Lewis acid sites. Additionally, in paper [24] the authors have compared the Fe-exchanged TiO_2-pillared montmorillonite doped with or without 1% CeO. Both samples had the same number of acid sites (more Brønsted acid sites than Lewis acid sites), which suggests that the surface acidity depends on the support and not the active material. In conclusion, the active material forms new acidic centres, however, especially the modification of the support decides about the acidity.

Obviously, the type of the ‘‘pillar’’ causes a change of the acidity. Chmielarz et al. [6] have compared the ZrO_2-, TiO_2- and Al_2O_3-pillared montmorillonite doped with cobalt or copper as active materials. The starting material was the montmorillonite from Wyoming. At 343 K the acidity of the Al_2O_3-pillared montmorillonite was 376.2 μmol/g and 1.48 μmol/m^2 but for the TiO_2-pillared montmorillonite—553.3 μmol/g and 1.98 μmol/m^2 [6], which suggests that the TiO_2 ‘‘pillar’’ results in a higher increase of the acidity than the Al_2O_3 ‘‘pillar’’. The introduction of the active material—

copper or cobalt to the Al_2O_3-pillared montmorillonite decreased the acidity by about 40% and in the case of the TiO_2-pillared montmorillonite only by ca. 10%. How does this change the influence of the acidity on the catalytic activity? The support whose acidity is larger increases its SCR reaction. And at 743 K the NO conversion of the TiO_2-pillared montmorillonite and the Al_2O_3-pillared montmorillonite are 98 and 80%, respectively. The promotion with cobalt increases the NO conversion by ca. 5% for both supports, thus the type of the ''pillar'' decides about the acidity and the activity more than the type of the active material.

Carvalho et al. [22] have characterized the acidity of the ZrO_2- and the Al_2O_3-pillared montmorillonite by two methods: the adsorption of pyridine and of 1-butene. The first method showed mainly the Lewis acid sites but the ZrO_2-pillared montmorillonite had more acid sites than the Al_2O_3-pillared montmorillonite.

To summarize each step of the preparation of the catalysts, acidic activation and ''pillaring'' change the acidity of montmorillonites, therefore the control of the preparation conditions is very important for the optimum results of the catalyst.

It is known that water and ammonia molecules have a very similar kinetic diameter [23] and it is possible that active sites of these molecules are the same. On the other hand, a water sorption decrease may be obtained through a replacement of the exchanged ions by the H_3O^+ ions and the removal of the Al^{3+}, Mg^{2+} or Fe^{2+} ions from the octahedral layer that causes its removal. The amount of the sorbed water vapour depends on the surface availability and the introduced active material. Each parameter of the catalyst preparation, such as the calcination temperature and/or the intercalation with hydroxycations influences the change of water adsorption. The temperature of calcination as a parameter of water adsorption on the Al_2O_3-pillared montmorillonite has been studied by Yamanaka et al. [24]. The comparison with silica gel and zeolites leads to the same results of all the materials. Zhu et al. [25] have described water adsorption on the alumina ions pillared montmorillonite and suggested that water adsorbs in large pores. Malla et al. [26,27] have compared the ZrO_2- and TiO_2-pillared montmorillonites with the Al_2O_3-pillared montmorillonites modified with Ca^{2+} ions. The hydrophilic properties due to the Ca^{2+} cations and porosity were attributed to the water sorption. However, Grzybek et al. [11] have suggested each step of the preparation: the intercalation with Al_2O_3 and the introduction of carbon deposits leads to a change in the hydrophilic properties of the Al_2O_3-pillared montmorillonite introduced by carbon deposits.

Numerous catalytic tests show that the presence of water in the reaction conditions affects the catalytic activity. Chmielarz et al. [28] have observed that the presence of water in the SCR reaction conditions decreases the NO conversion by about 2% for the TiO_2-pillared montmorillonite promoted by a copper catalyst, but the removal of water from the gas mixture causes a return to the prior value. This suggests that water molecules are sorbed by the physical sorption. This effect is not practically observed when the catalyst has a lower acidity (Al_2O_3-pillared montmorillonite).

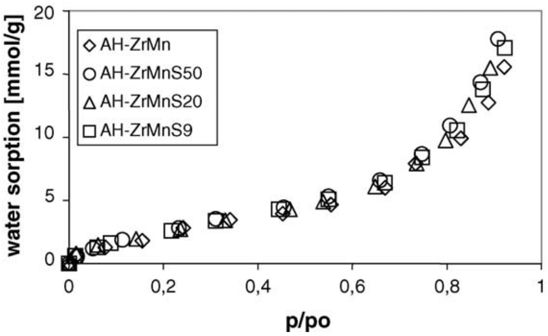

Fig. 5. Adsorption of water vapour (mmol/g) at 298 K for catalysts based on AH-Zr with a different weight ratio of manganese to saccharose.

The isotherms of vapour water adsorption as an example of the series of acid treated ZrO_2-pillared montmorillonite is shown in Fig. 5. All the isotherms belonged to the second type of the IUPAC classification. The sorption on the AH-ZrMnS9 sample is bigger than on the AH-Zr, so MnO_x has increased the H_2O sorbed amount. Additionally, all the catalysts studied here have similar specific surface areas, which suggests that saccharose has not influenced the amount of the water sorption sites. All the samples based on the acid pre-treated ZrO_2-pillared montmorillonite doped with MnO_x have the same amount of water vapour sorption sites.

To sum up, water is bonded by van der Waals forces. In the presence of ammonia it is removed and replaced with ammonia molecules and it does not influence the catalytic activity.

4. Conclusions

Taking into account the above-mentioned results of the acidity, and the hydrophilic and catalytic activity, the following conclusions can be made:

- The acidity of the catalysts is determined by the acidity of the support, and not by the MnO_x active material. The preliminary acidic activation of support (with the 20% HCl) results in stronger acidic centers. The ammonia sorption on the acid modified support leads to a change of its surface, thus forming new acid sites. At a higher temperature the coverage of the surface by ammonia monolayer is thinner than at a lower temperature.
- The acidity of the support decides about the catalytic properties. The acid treated support promoted with MnO_x results in a better NO conversion of the catalyst. Ammonia molecules are more strongly bonded on the acid activated support surface.
- The active material: manganese oxides/hydroxides distributed in small clusters or a single ion form are not acidic centers.
- Water vapour adsorption on a pillared clay does not depend on the preparation of samples. The introduction of manganese oxides does not influence water adsorption. The presence of saccharose in the promoting solution does not change the hydrophilic properties of catalysts, either.

The method of the subsequent ammonia adsorption measured by isotherms may explain the change in surface acidity.

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