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The Influence of Montmorillonite Treatment on Structure, Sorption Properties and Catalytic Behaviour: Part I. Zirconia Pillared Clays Modified with Manganese as Denox Catalyts

by T. Grzybek[1*], J. Klinik[1], D. Olszewska[1], H. Papp[2] and J. Smarzowski[1]

[1]*Faculty of Fuels and Energy, University of Mining and Metallurgy,*
Al. Mickiewicza 30, 30-059 Krakow, Poland
[2]*Lehrstuhl für Technische Chemie, Faculty of Chemistry and Mineralogy, University of Leipzig,*
Linnestr 3, 04103 Leipzig, Germany

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Clays were pillared with zirconium aquahydroxycations starting from untreated or HCl-pretreated montmorillonite. The supports were promoted with manganese by adsorption method. Structure and texture was studied by XRD and low temperature argon sorption. The information on distribution of manganese was obtained from XPS and textural studies. Catalytic activity in SCR reaction was shown to depend on the initial pretreatment of montmorillonite. Selectivity to nitrogen was connected with the distribution of active material.

Key words: catalysis, adsorption, selectivity, synthesis

Selective catalytic reduction by ammonia (DeNOx) is the only method used on industrial scale for removal of nitric oxide from flue gases from stationary sources [1]. The industrially used catalyst is V_2O_5-TiO_2 promoted with WO_3. Several other types of catalysts were also proposed for the SCR reaction, mainly oxides/hydroxides of iron, copper, chromium and manganese on traditional supports, such as silica or alumina [1,2] or active carbons [3,4]. Catalysts based on natural clays have raised considerable interest lately, because of several possibilities of modification of their properties, both structural, textural and chemical, *e.g.* acid/base properties [5]. It was reported by Yang *et al.* that titania pillared montmorillonites promoted with chromium had higher activity than that of industrially used catalysts [6]. Similarly, so-called delaminated montmorillonites were shown to be good catalysts [7]. Moreover, Fe^{3+} promoted titania pillared montmorillonites had higher activity in the presence of SO_2 and H_2O than in the absence of these substances, which is of considerable importance because these gases lead often to deactivation of the catalysts [8].

The subject of this work was to study the influence of different preparation parameters on structure, sorption properties and SCR activity of Al- or Zr-pillared

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[*] Author for correspondence.

montmorillonites promoted with manganese. Part I considers zirconia-pillared clays and the influence of montmorillonite pretreatment on activity and selectivity in DeNOx reaction.

EXPERIMENTAL

Preparation of the catalysts: The basis material for the prepared samples is bentonite from Jelsovy Potok (Slovakia) from which montmorillonite was separated through sedimentation and used either without further cleaning, despite the fact, that it contained considerable amounts of iron oxides and calcium carbonate (M1, M2 or M3) or in a purified form obtained by the use of the method of Jackson *et al.* (M4) [9,10]. The bulk composition of the starting montmorillonite obtained by sedimentation is given in Table 1. Fig.1 shows the scheme of preparation steps. Montmorillonite was used either in untreated or HCl pretreated form (Table 2). Pillaring was carried out with an aqueous solution of zirconyl chloride under the following conditions: cation to montmorillonite ratio: 10 mmol/g; aging of pillaring solution 1 day at 353 K; pillaring one day at 353 K and 3 days at 298 K. So obtained supports were designated SZr-x (x – number of the support, 1 to 5; see Table 3). Zr-pillared montmorillonites were calcined and then promoted with manganese using adsorption method and the solution of manganese(II) nitrate(V) in water-saccharose solution. The choice of such medium was prompted by the article of Boot *et al.* [11] who showed that the addition of saccharose led to the introduction of manganese on the whole surface of ZrO_2 support, while its removal resulted in preferential formation of bigger manganese – containing deposits on the outer surface of the grains of the support. For comparison, montmorillonite was treated with zirconium nitrate aged only 2 hours, which cannot be expected to lead to pillaring (SZr-6). Manganese was introduced onto this support by wet impregnation from the solution of manganese(II) nitrate in water. The designation of the catalyst is constructed of the name of the support by adding Mny (where y = amount of introduced active material in wt.%). The preparation data and designation of the catalysts is given in Table 3.

Table 1. Bulk composition of the starting montmorillonite (M1) as given by XRF [wt.%].

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
2.48	3.23	18.90	58.69	0.05	0.36	0.18	0.21	0.08	3.54

Table 2. The list of montmorillonites used for pillaring and the preparation of catalysts.

Sample	M1[1)]	M2[1)]	M3[1)]	M4[2)]	M5[2)]
Sedimentation time [min]	15	15	15	42	42
Pretreatment	–	20% HCl, 1 h 369 K	20% HCl, 4 h, 369 K	–	20% HCl, 4 h, 369 K

Starting material: [1)]bentonite from Jelsovy Potok, Slovakia; [2)]montmorillonite purified of calcium carbonate and iron oxides by the method of Jackson [10].

Characterization: In order to elucidate the structure of the supports and catalysts the following features were analyzed:

- texture of chosen samples by low temperature argon sorption using a standard volumetric equipment,
- structure by X-ray diffraction using Philips ADP X`Pert diffractometer and CuKα radiation for calcined samples (if not stated otherwise) oriented on a glass plate,
- surface composition of the supports and catalysts, as well as manganese distribution by X-ray photoelectron spectroscopy. The spectra were recorded with a Leybold AG spectrometer equipped with a MgKα source and a multichannel plate analyzer working in FAT mode (ΔE = const) at a pass energy of 29.6 eV. The samples were studied in the form of pellets loosely packed onto the sample holder. The pressure in the main chamber was better than 3×10^{-8} Tr. The spectra were smoothed, a non-linear back-

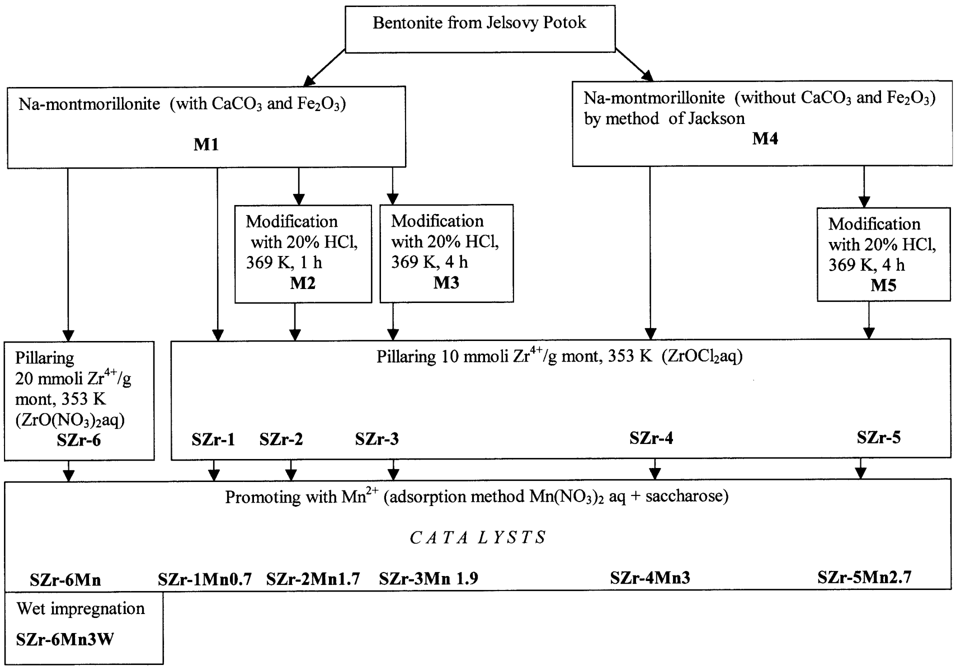


Figure 1. The scheme of preparation steps.

ground was subtracted and the fitting was carried out with a 50/50 convolution of Lorentz and Gauss curves. Al 2p at a binding energy of 74.2 eV (typical for montmorillonites [12]) was used as a calibration standard. The calibration peak was checked against C 1s at 284.6 eV, but it was too small in some cases and could not be used consequently for all spectra. The composition of the samples was calculated using the areas of the appropriate peaks and the sensitivity factors of Wagner *et al.* [13].

Table 3. The preparation data and designation of the samples.

Sample	Smectite isolated by method of Jackson [10]	Pretreatment of smectite	Montmorillonite pillaring agent	Mn introduction method	Mn content [wt %]
Bentonite	–	–	–	–	–
M1	–	–	–	–	–
M2	–	$+^{a)}$	–	–	–
M3	–	$+^{b)}$	–	–	–
M4	+	–	–	–	–
M5	+	$+^{b)}$	–	–	–
SZr-1	–	–	$M1/Zr^{d)}$	–	–
SZr-2	–	$+^{a)}$	$M2/Zr^{d)}$	–	–
SZr-3	–	$+^{b)}$	$M3/Zr^{d)}$	–	–
SZr-4	+	–	$M4/Zr^{d)}$	–	–
SZr-5	+	$+^{b)}$	$M5/Zr^{d)}$	–	–

Table 3 (continuation)

SZr-6	–	–	M6/Zr[c)]	–	–
SZr-1Mn0.7	–	–		A	0.7
SZr-2Mn1.7	–	+[a)]		A	1.7
SZr-3Mn1.9	–	+[b)]		A	1.9
SZr-4Mn3	+	–		A	3.0
SZr-5Mn2.7	+	+[b)]		A	2.7
SZr-6Mn3W	–	–[c)]		W	3.0

[a)] 20% HCl, 1 h, 369 K; [b)] 20% HCl, 4 h, 369 K; [c)] pillaring 20 mmol Zr^{4+}/g mont, 353 K ($ZrO(NO_3)_2aq$); [d)] pillaring 10 mmol Zr^{4+}/g mont, 353 K ($ZrOCl_2aq$); A – adsorption with $Mn(NO_3)_2$ + saccharose in water; W – wet impregnation.

Catalytic behaviour: Catalytic performance was studied in a fixed bed microreactor under the following conditions: reaction mixture composition: 800 ppm NO and NH_3, 6% O_2 in helium; flow: 50 ml/min; mass of catalyst 200 mg; temperature 413 to 693 K; educts and products analysis by NDIR or gas chromatography. Before each catalytic experiment the sample was dried on line in helium at 393 K for 1 hour (flow = 100 ml/min) and calcined at 523 K for two hours in a mixture of 3% O_2 in helium (flow 100 ml/min).

RESULTS AND DISCUSSION

Texture: Fig. 2 shows argon sorption isotherm as an example for SZr-2. The isotherms for all samples are predominantly of type I according to IUPAC classification which stresses their microporous character. The sorption data were used to calculate specific surface area according to BET procedure (S_{BET}), the volume of micropores V_{mic} from the amount adsorbed at $p/p_o = 0.3325$ and the volume of mesopores V_{mes} from a second variant of Dubinin's method (Table 4). From Table 4 it may be seen that short aging times of 1 day are enough to obtain high specific surface areas in the case of zirconium pillared clays. There is no difference in textural parameters for supports obtained from untreated or HCl-pretreated montmorillonite. The time of HCl pretreatment did not influence textural parameters. The introduction of manganese onto untreated support did not lead to any change in S_{BET}. On the other hand, after Mn modification of HCl-pretreated support, S_{BET} decreased by *ca.* 30%.

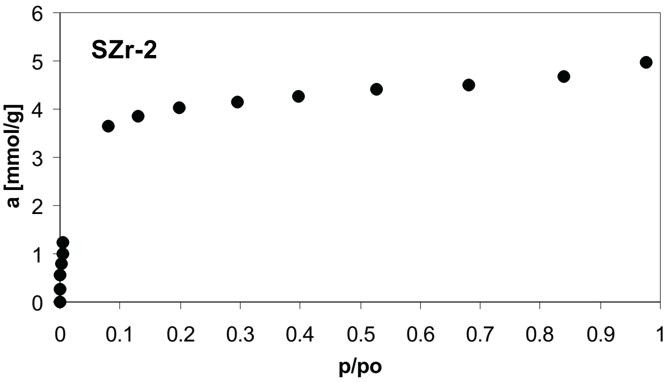


Figure 2. Argon sorption isotherm for support SZr-2.

Table 4. Specific surface area S_{BET} and micropore V_{mic} or mesopore V_{mes} volumes for the studied Zr-pillared samples.

Sample	SZr-1	SZr-2	SZr-3	SZr-1Mn0.7	SZr-3Mn1.9	SZr-6Mn3W
S_{BET} [m^2/g]	300	312	306	313	222	73
V_{mic} [cm^3/g]	0.15	0.07	0.10	0.12	n.m.	n.m.
V_{mes} [cm^3/g]	0.03	n.m.	0.08	0.03	n.m.	n.m.

n.m. – not measured.

Structure: Fig. 3a, b and c show XRD spectra for selected unpillared and Zr-pillared clays. In the text, specimen introduced onto a glass slide in: a) a calcined form are designated without an asterics (*e.g.* SZr-1), b) a noncalcined form with an asterics (*e.g.* SZr-1*), while those introduced in a noncalcined form and then calcined *in situ* have two asterics in their designation (*e.g.* SZr-1**). The structural parameter, which allows to determine the pore size in the direction perpendicular to clay layers (the basal spacing d_{001} calculated from the first low-angle peak), is shown in Table 5. From Table 5 and Fig. 3 it may be seen that pillaring with zirconyl chloride resulted in structures amorphous to XRD when calcined samples were studied, independent of the fact if the starting smectite was pretreated with hydrochloric acid solution or not. The lack of a low-angle peak at a relevant θ region points to the disappearance of long-range ordering in c direction. Near-range ordering in b direction was, however, not affected as it was possible to register the peak corresponding to d_{020} at typical 4.48 nm. Due to the disappearance of the low angle peak characteristic for non pillared smectite, this may indicate successful pillaring, with the formation of a so-called delaminated structure. Additional proof of pillaring is connected with the formation of high surface area of so-obtained calcined samples (*ca.* 300 m^2/g) in comparison to nonpillared calcined smectite (41 m^2/g [14]). A positive proof of the introduction of pillars was given by Chmielarz *et al.* [14] who showed that noncalcined montmorillonite pillared with Zr (corresponding to sample SZr-1) oriented on a glass plate showed XRD peak corresponding to d = 1.96 nm. The same procedure, *i.e.* the measurements of X-ray diffractograms for noncalcined oriented SZr-4* and SZr-5*, prepared from motmorillonite purified of iron oxide and calcium carbonate showed distinct peaks corresponding to basal spacing d_{001} of 2.25 and 1.96 nm, respectively. The calcination *in situ* of a layer oriented on a glass plate led to the considerable broadening of XRD pictures and a decrease in d_{001} to 1.96 and 1.63, respectively (cp. Fig. 3b).

Surface composition: XPS spectrum is shown as an example for SZr-4Mn3 in Fig. 4 O 1s, Si 2p and Al 2p peaks at respectively 531.8, 102.6 and 74.5 eV are at positions typical for montmorillonites [12]. The binding energies of the Zr 3d peaks (182.7 and 185.1 eV) point to ZrO_2 [15]. A manganese 2p peak was only found for SZr-6Mn3W at 642.1 eV. It may be interpreted as Mn^{3+}or Mn^{4+} [16–18]. The multiplet splitting of the Mn 3s peak was 5.5 eV, which according to Murray *et al.* [18] may be interpreted as the presence of Mn_3O_4. For all other catalysts, Mn 2p peaks have been below detection level.

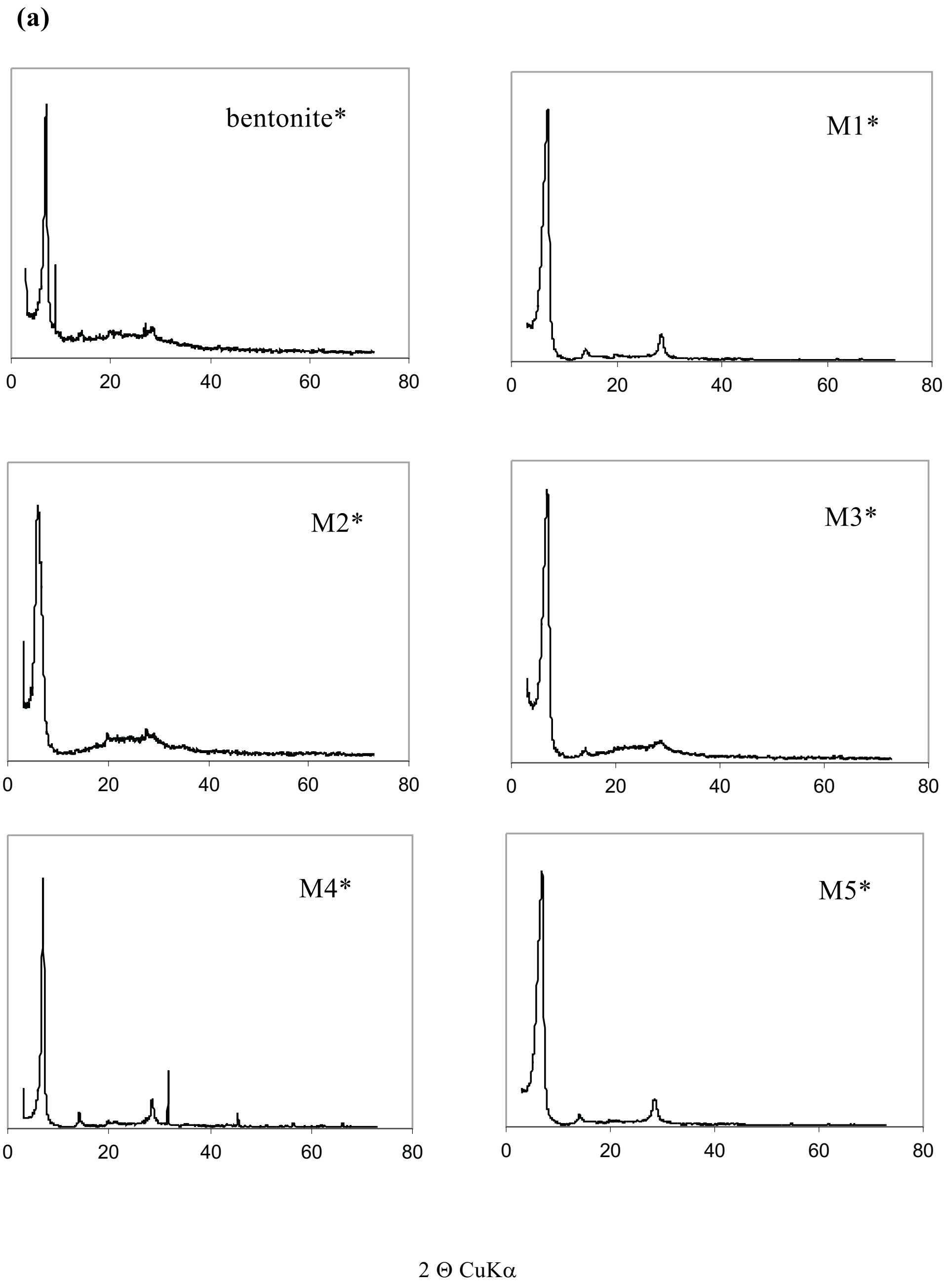


Figure 3. XRD spectra for: (a) unpillared clays (noncalcined); (b) Zr-pillared clays on the basis of sedimented montmorillonite or montmorillonite purified by the Jackson method (noncalcined); (c) Zr-pillared clays (calcined before the preparation of the glass slide – without asterics, or calcined *in situ* on a glass slide **).

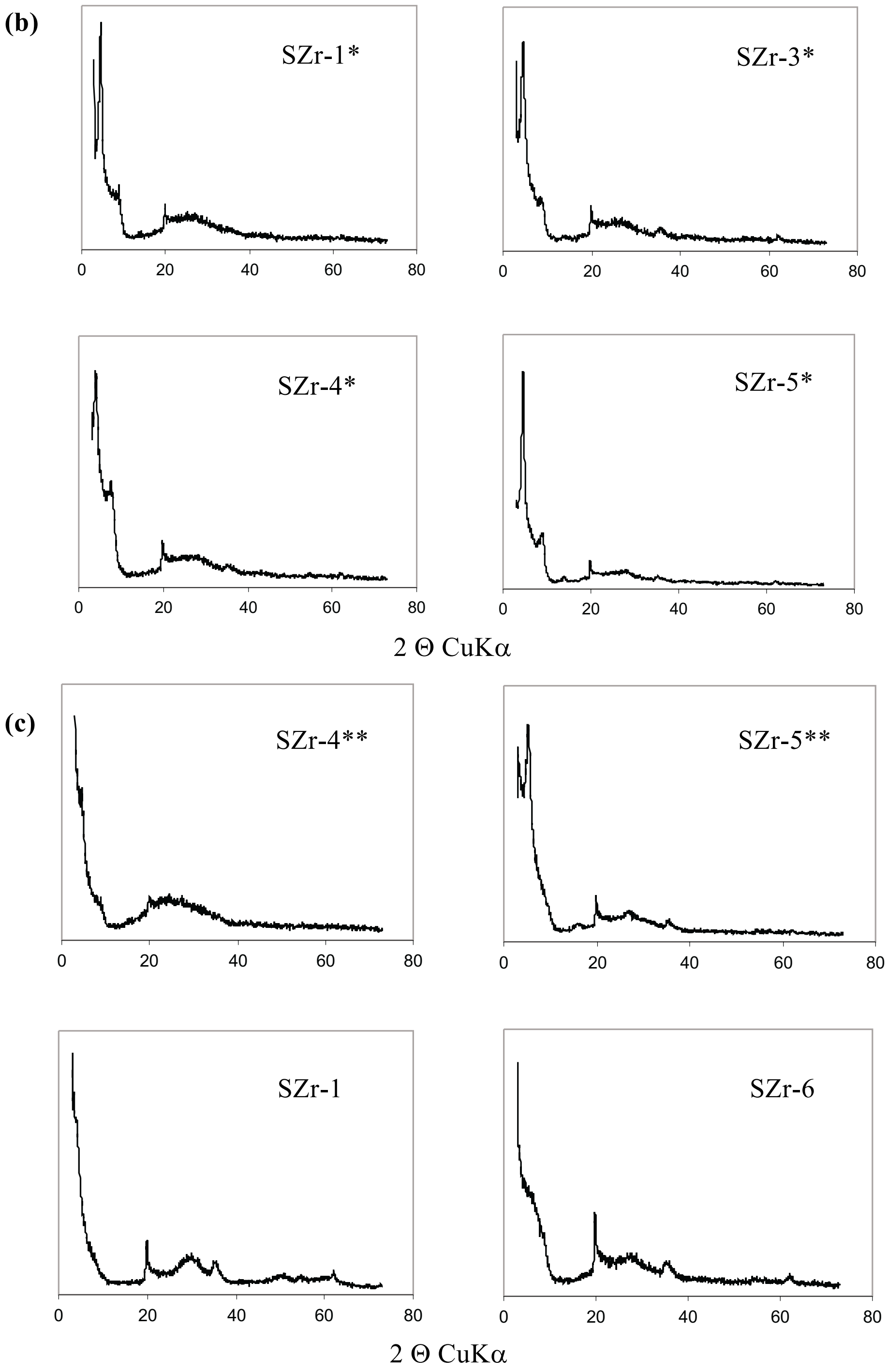


Figure 3. (continuation).

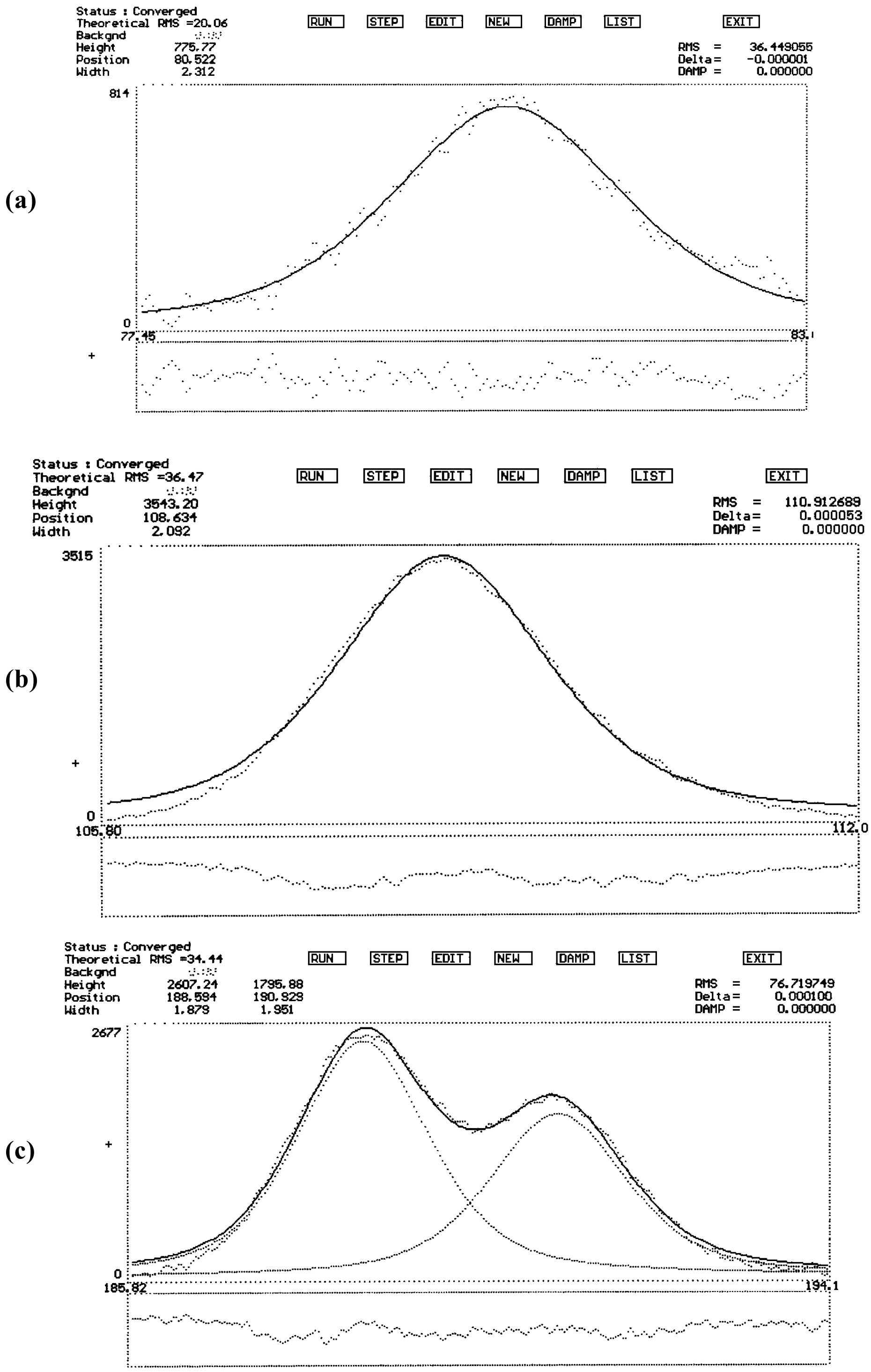
Table 5. Basal spacings d_{001} for the studied nonpillared and Zr-pillared samples.

Sample noncalcined	M1*	M2*	M3*	M4*	M5*	SZr-1*	SZr-2*	SZr-3*	SZr-4*	SZr-5*	SZr-6*
d_{001} [nm]	1.26	1.47	1.53	1.26	1.30	1.96	n.m.	1.96	2.25	1.96	n.m.
Sample calcined *in situ*	M1**	M2**	M3**	M4**	M5**	SZr-1**	SZr-2**	SZr-3**	SZr-4**	SZr-5**	SZr-6**
d_{001} [nm]	n.m.	n.m.	n.m.	0.98	0.98	n.m.	n.m.	n.m.	1.96	1.63	n.m.
Sample calcined	M1	M2	M3	M4	M5	SZr-1	SZr-2	SZr-3	SZr-4	SZr-5	SZr-6
d_{001} [nm]	1.25	n.m.	n.m.	◆	◆	◆	◆	◆	n.m.	n.m.	◆

n.m. – not measured; ◆ – delaminated structure.

Surface composition for the samples under study is given in Table 6. From Table 6 it may be seen that:
(i) acidic treatment of the initial montmorillonite led to a decrease in the surface Al content (cp. Al:Si ratio respectively for SZr-2, SZr-2Mn1.7, SZr-3Mn1.9 and SZr-4Mn3: 041; 0.37; 0.19; 0.27) and different Zr:Si ratios (0,40; 0.39, 0.45 and 0.48, respectively for SZr-2, SZr-2Mn1.7, SZr-3Mn1.9 and SZr-4Mn3). Different Zr:Si ratios obtained after pillaring of untreated or acidic pretreated montmorillonite may be connected with some ZrO_2 precipitated on the samples. Chmielarz *et al.* showed [14] that the bulk amount of zirconium was much higher when untreated montmorillonite was pillared in comparison with pillaring of HCl pretreated montmorillonite under the same conditions (Zr:montmorillonite ratio; OH:Zr ratio; aging times and time and temperature of pillaring), and (ii) the adsorption method led to the formation of small Mn clusters. Bigger crystallites precipitated mostly on the outer surface of support particles after wet impregnation. This conclusion is based on XPS and textural studies. For SZr-6Mn3W high intensity ratios of Mn 2p to Zr 2p or Mn 2p to Al 2p peaks of respectively 9.32 and 8.6 were registered, which greatly exceed XPS ratios calculated for a monolayer coverage. On the other hand, no recognisable Mn 2p peak was found for SZr-1Mn0.7, SZr-2Mn1.7 and SZr-3Mn1.9 samples, which points to a depletion of the samples in Mn on the outer surface of the studied support particles. This means that manganese was deposited inside the porous system and did not form any bigger crystallites on the outer surface. This argument is backed by the values of specific surface area, which are within experimental error (*ca.* 10% accuracy) for SZr1-Mn0.7 and *ca.* 30% lower for SZr-3Mn1.9 than for the appropiate support. This excludes precipitation of any bigger crystallites of MnO_x within the pores as precipitates of *e.g.* 1 nm would lead to the blocking of micropores, and thus resulted in very small S_{BET}.

Catalytic behaviour: NO conversion for the studied catalysts is given in Fig. 5. Selectivity to N_2 was *ca.* 100% for all the samples depicted in this figure, except for SZr-6Mn3W, where it was 87–55% for temperatures between 453–639 K (not shown in Fig. 5).



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Width            2.312
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DAMP =       0.000000
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RMS   =     76.719749
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Figure 4. XPS spectrum for SZr-5: (a) Al 2p, (b) Si 2p, (c) Zr 3d, (d) O 1s.

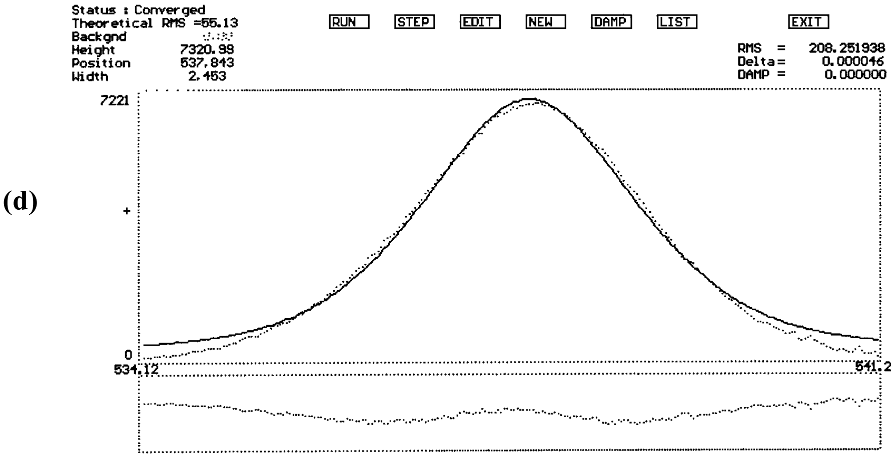

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Figure 4. (continuation).

Table 6. Surface composition of the samples studied. Al + Si + (Zr) + O + Mn = 100 at. %.

Sample	Surface composition (at. %)				
	Al	Si	Zr	O	Mn
M1	8.7	21.7	–	69.6	–
M4	10.4	22.2	–	67.4	–
SZr-1	7.0	17.1	6.8	69.1	–
SZr-5	7.4	22.4	3.4	66.6	–
SZr-1Mn0.7	6.4	17.4	6.7	69.5	$^{5)}$
SZr-2Mn1.7	3.4	17.5	7.9	71.2	$^{5)}$
SZr-3Mn1.9	5.3	19.6	9.5	65.6	$^{5)}$
SZr-6Mn3W	6.8	16.8	1.4	69.4	5.6

$^{5)}$under detection level.

From Fig. 5 it may be seen that: (i) in contrast to active carbon based catalysts [19] and in agreement with carbon modified montmorillonites [14], activity increased with temperature, (ii) there is no correlation between specific surface area of manganese promoted catalysts and their activity towards NO reduction by ammonia (cp. SZr-1Mn0.7 and SZr-3Mn1.9 with S_{BET} of 313 and 222 m^2/g, respectively); although specific surface area is smaller for acid pretreated montmorillonites, the activity is much higher; (iii) additional purification of montmorillonite by the method of Jackson did not lead to the improvement in catalytic activity, (iv) acid pretreated montmorillonites led to more active catalysts than untreated ones. Similar observations were made by Yang *et al.* [20] for iron promoted titania pillared clays. Moreover, the duration of acidic pretreatment influenced activity, and (v) small clusters of Mn did not produce N_2O in contrast to larger Mn deposits. Similar observations were made for active carbons [19] or montmorillonites covered with carbon promoted with

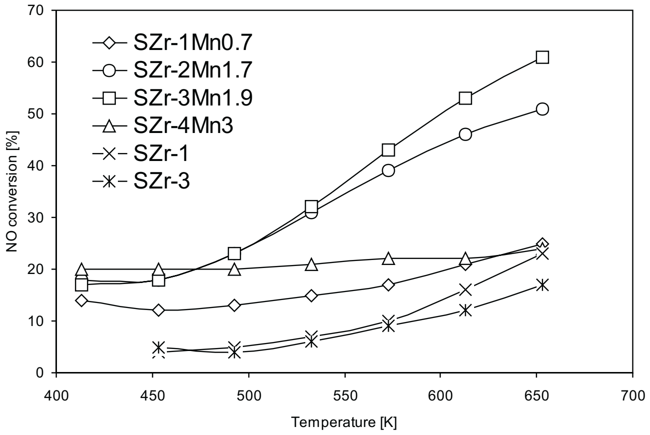

Figure 5. NO conversion for the catalysts under study.

manganese oxides/hydroxides [14,21]. Therefore, it may be concluded that the temperature dependence of activity is connected with the type of the support but the increased production of N_2O at higher temperatures was mostly or exclusively influenced by the size of manganese deposits.

CONCLUSIONS

Pillared smectites promoted with manganese oxides/hydroxides were prepared basing on untreated or HCl-pretreated smectites.

It was found that:

- Initial pretreatment does not influence textural and structural properties of the obtained supports.
- The XRD experiments for the obtained samples point to so-called delaminated structure.
- Catalytic activity in the reaction of nitric oxide reduction with ammonia and selectivity to nitrogen did not depend on textural properties. On the other hand, strong influence of acidic pretreatment of the starting material was found.
- Selectivity to nitrogen was dependent on the distribution type of active material.

Acknowledgments

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