Pillared smectite modified with carbon and manganese as catalyst for SCR of NO_x with NH_3.

Part I. General characterization and catalyst screening

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Carbon- and manganese-modified zirconia-pillared smectites were prepared, characterized (XRD, BET and pore analysis, XPS) and tested in selective catalytic reduction of NO_x with NH_3. Both untreated and acidic pretreated smectites were used. The acid pretreatment increased NO conversion and influenced the extent of carbon introduction into the porous system. The carbon deposit improved selectivity of the catalytic reduction to N_2.

Keywords: SCR, texture, XRD, smectites, carbon deposits

1. Introduction

Selective catalytic reduction of nitrogen oxides with ammonia is at present the only economically realistic choice for the cleaning of stack gases from stationary sources [1,2]. The catalyst used in industry (vanadium oxide on titania promoted with tungsta) operates at medium temperature region but some other proposed catalysts were shown to have optimum performance at low (ca. 393–523 K) or high temperatures (above ca. 673 K). The examples of the former are promoted active carbons [2–5] and of the latter silica–aluminas [6–9]. The low-temperature region below 573 K is especially interesting because the production of dinitrogen oxide in a side reaction increases with temperature. It must be, however, stated that active carbons have some unfavourable features, among others fairly narrow porosity which may result in considerable diffusion limitation, as well as not too high mechanical stability expressing itself in considerable attrition and difficulty in formation of industrially favourable monoliths. These difficulties might be avoided by using composite materials based on silica–alumina basis and modified with carbon.

The subject of this work was to study zirconia-pillared smectite modified with carbon and promoted with manganese as catalyst for SCR.

2. Experimental

2.1. Catalysts

The starting material was smectite from Jelsovy Potok (Slovakia) the composition of which is given in table 1. Either its sodium form (A1) or the sample treated with 20% HCl (at 369 K for 4 h) (A2) was pillared with zirconia using an aqueous solution of zirconyl chloride (10 mmol Zr/1 g of smectite), thus giving samples M1 and M2. The solution of oligocations was aged for 1 day at 353 K and the pillaring was carried out at 353 K for 1 day and at 293 K for 3 days. Chloride anions were then removed by washing and centrifugation. Subsequently, the samples were modified with polymer in a way described for alumina-pillared clays by Grzybek et al. [10]. The suspension of 100 ml of 2.5% aqueous solution of commercial polyacryloamide (Gigtar) and 1 g of noncalcined smectite were mixed for 1 h at room temperature, left without mixing at 296 K for additional 24 h and then dried at 338 K in air. Then the samples were pelletized without the addition of binder and carbonized under nitrogen flow at 773 K for 30 min, thus giving M1C and M2C. Similarly prepared alumina-pillared montmorillonites were shown to possess islands of carbonaceous material both on the outer and inner surface of the inorganic support [10]. Bulk composition of pillared samples modified with polymer was determined by XRF and is given in table 2. The amount of introduced carbonaceous deposit was estimated from thermoprogrammed oxidation experiment TPD from the amount of desorbed carbon dioxide to be 0.5 and 0.3 wt% for M1C and M2C, respectively. Manganese was introduced by an adsorption method from aqueous solution containing manganese(II) nitrate and saccharose (the weight ratio of Mn to saccharose = 9.2) at 353 K. The addition of saccharose to the preparation solution was prompted by the article of Boot et al. [11] who showed its positive influence on the formation of smaller manganese deposits on zirconia. The obtained catalysts

Table 1
The composition of smectite from Jelsovy Potok given by XRF.[a]

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	0.07	0.20	0.08	3.54

[a] LOI (loss on ignition at 1273 K) 12.4 wt%.

Table 2
Bulk composition of pillared clays M1C and M2C as given by XRF.[a]

Sample	Na_2O	MgO	ZrO_2	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
M1C	0.29	1.90	29.98	10.75	38.38	6.30	0.25	0.07	0.16	0.04	2.41
M2C	0.15	1.79	4.66	11.20	66.84	3.86	0.42	0.14	0.29	0.04	1.83

[a] TG mass loss on heating at 1273 K: M1C 8.45 wt%, M2C 8.41 wt%.

were designated M1CMnxx and M2CMnxx, where xx denotes the amount of introduced manganese (by weight).

Additionally, pillared smectites nonmodified with carbon were studied (M1 and M2). For comparison, M1 was also promoted with Mn after calcination in air at 773 K for 3 h in a similar way to that used for carbon-modified samples (designation M1Mnxx).

2.2. Structural and textural characterization

The structure of nonpillared smectites A1 and A2 and pillared forms either not modified or modified with carbon (M1, M1C and M2C) was determined by XRD using a Philips APDX'Pert diffractometer on oriented samples, prepared by spreading of the suspension of a sample onto the glass slide and drying it at room temperature. A1 and A2 were studied as noncalcined specimen, M1 in calcined and noncalcined form and M1C, M2C and M1Mn07 for the samples calcined before the preparation of glass slides. Texture was studied for pillared clays by low-temperature argon sorption (78 K) using a standard volumetric equipment. Surface composition, as well as distribution of manganese, were studied by X-ray photoelectron spectroscopy for selected samples using a Leybold AG spectrometer equipped with Mg K_α source and a multichannel plate analyzer working at pass energy of 29.6 eV. The samples were studied in the form of particles loosely packed onto the sample holder. The pressure in the main chamber during experiments was better than 3×10^{-8} mbar. The spectra were smoothed and a nonlinear background was subtracted. The spectra were fitted with a convolution of 50 : 50 Lorenzian and Gaussian curves. The C 1s peak at 284.6 eV was used to calibrate binding energies. The content of elements was calculated using the area of the peaks and sensitivity factors of Wagner et al. [12].

2.3. Catalytic tests

Catalytic activity and selectivity were studied in a fixed-bed reactor under the following conditions: temperature range of 373–723 K (in intervals of 50 K), reaction mixture composition 0.25% NO and NH_3, 2.5% O_2 and the rest helium, mass of the catalyst 200 mg, flow 40 ml/min.

Table 3
Textural parameters: specific surface area S_{BET}, volume of micropores V_{mic} and volume of mesopores V_{mes} for the studied samples.

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)
A1	41	n.m.[a]	n.m.
A2	190	n.m.	n.m.
M1	300	0.15	0.03
M1C	182	0.07	0.03
M2	306	0.10	0.08
M2C	287	0.12	0.06
M1Mn07	313	0.12	0.03
M1CMn16	171	0.07	0.03
M2CMn14	189	0.08	0.06
M2CMn5	293	0.12	0.06

[a] n.m. – not measured.

The concentration of educts and products NO, NH_3, O_2, N_2, N_2O, H_2O, NO_2 and CO_2 was determined using a mass spectrometer VG 200 SX in the channeltron mode of detection. The error of the determination of NO conversion was ±0.5% and selectivity to N_2 was ±1.5%.

Before catalytic tests the samples were outgassed on stream up to 723 K.

3. Results and discussion

3.1. Characterization of the studied catalysts

Argon sorption isotherms are of type I according to BET classification for all studied samples. The parameters calculated from the isotherms: specific surface area S_{BET} according to the BET procedure, volume of micropores V_{mic} and volume of mesopores V_{mes} estimated from the amount sorbed respectively at $p/p_0 = 0.3225$ and 1, are summarized in table 3.

From table 3 it may be seen that:

(i) The specific surface area of montmorillonite after acidic pretreatment (A2) increased to 190 m^2/g (cf. untreated montmorillonite $S_{\mathrm{BET}} = 41$ m^2/g). Similar effects were observed for montmorillonites treated with sulphuric acid and were explained by partial precipitation of SiO_2 from smectite structure to form deposits between the layers [13].

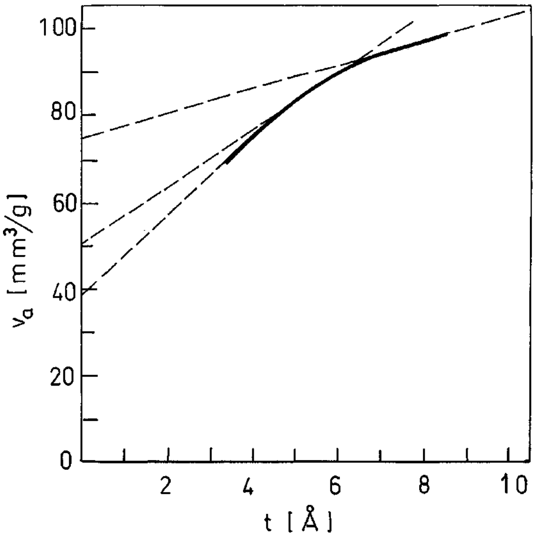


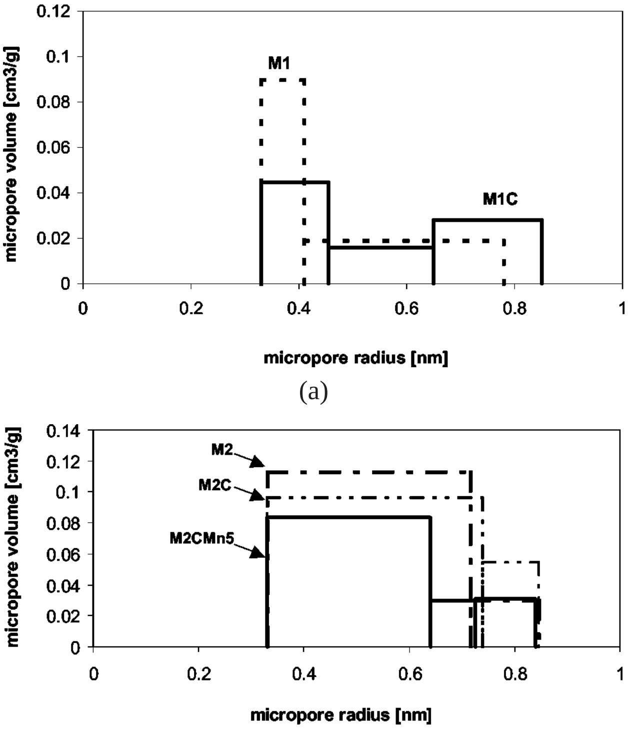
Figure 1. t curve for M1C catalyst. Solid line – experimental results.

(ii) Smectites both untreated and treated with HCl undergo pillaring to form samples with similar texture, predominantly microporous with specific surface area of ca. 300 m^2/g.

(iii) The extent of modification with carbon depends on the surface structure of the starting samples. The decrease in specific surface area for M1 is much higher than for smectite initially treated with HCl (M2). Similar observations may be made for the decrease in micropore volume.

(iv) The textural parameters do not change, within experimental error, after the introduction of Mn for M1 series but S_{BET} and V_{mic} somewhat decrease for higher amounts of Mn introduced onto the M2C sample.

As the catalysts are predominantly microporous, the analysis of micropore volume by the Brunauer method was carried out basing on the t curve [14,15]. A typical t curve is shown in figure 1 for the M1C catalyst. It may be seen from the figure that the prolongation of the t curve towards 0 value of adsorbed layer thickness does not cross the figure at the point 0,0 but at the value of adsorbed volume of ca. 38 mm^3/g. This indicates that the catalyst contains submicropores, i.e., pores where the formation of a full adsorbed layer on each wall is not possible and thus the radius of pores is smaller than 0.33 nm (Ar atom diameter). Figure 2 (a) and (b) shows volumes of micropores with radii of 0.33–0.85 nm for samples modified with carbon and promoted with manganese for the M1 and M2 series. The introduction of polymer into M1 leads to a decrease in the amount of smallest micropores ($r = 0.33$–0.41 nm) almost by half. The distribution of pores in sample M2 is distinctly different. Almost no change in the slope of t curve for pores with radii between 0.33 and 0.72 nm indicates their more homogeneous structure. The interaction with polymer decreases the volume of these pores by only ca. 20%. The introduction of manganese leads to further small decrease in this value, although the pores get somewhat narrower which is possibly connected with some preferential distribution of manganese in broader micropores.



(a)

(b)

Figure 2. The distribution of micropores as a function of their radii: (a) M1 and (b) M2 series.

It may be therefore conluded that carbon deposit covered the inner walls of micropores and/or their inlets for samples based on untreated smectite. The modification of the starting smectite with hydrochloric acid solution inhibited the covering of micropores with carbon film. The fact that either no difference or only a small decrease in specific surface area and micropore volume were observed after manganese introduction allows the conclusion that it was deposited on the inner surface in the form of small clusters or individual cations. The presence of larger crystallites of manganese on the outer may be excluded due to the lack of a Mn 2p peak (see further).

Figure 3 shows XRD spectra of noncalcined M1, calcined M1Mn07, M1C and M2C catalysts and for comparison, A1 and A2 (also noncalcined). The first peak observed in the spectra for A1, A2 and M1 is connected with diffraction from 001 layers of smectite. The structural parameter, changing during modification of smectites is the basal spacing d_{001} which was calculated from the position of the first low-angle diffraction maximum and is 1.29, 1.55 and 1.96 nm, respectively, for A1, A2 and M1. Acidic treatment does not lead to an extensive deterioration of the smectite structure which may be proven by the fairly narrow XRD peak. The fact that d_{001} is somewhat higher for A2 than A1 seeems to back the conclusion of Shinoda et al. [13] that some silica is deposited between the layers, in agreement with the increase in specific surface area. After

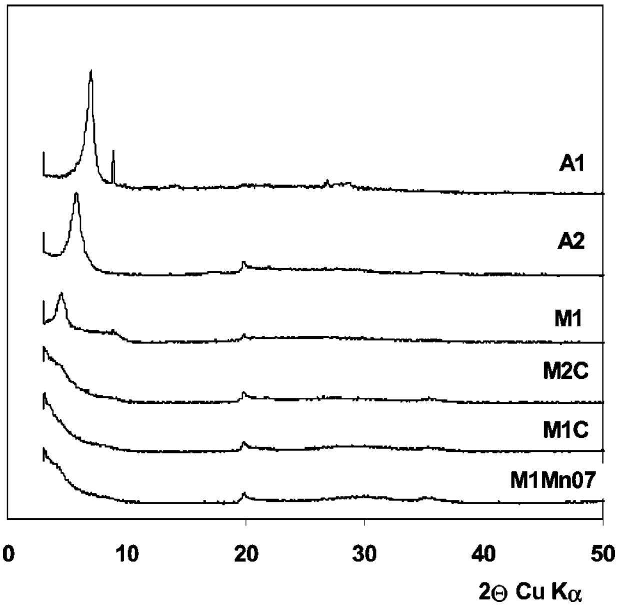


Figure 3. XRD spectrum of catalysts M1, M1Mn07, M1C and M2C in comparison to nonpillared A1 and A2.

pillaring d_{001} increases which proves successful pillaring (cf. M1). The calcination procedure results in the disappearance of the above mentioned maximum which may be interpreted as the disappearance of long distance ordering in the c-direction. The next peak observed in the spectrum corresponding to diffraction from 020 layers is in a position typical for montmorillonites and proves that the structure of the smectite layer is not disturbed. Pillaring, however, took place as peaks for nonpillared A1 and A2 are absent, as well. The observed lack of ordering in the c-direction is therefore a result of calcination and may be due to either very small crystallites formed or delamination. Such delaminated formations called "house of cards" were observed, e.g., by Chen et al. for iron-oxide-pillared bentonites [16]. XRD alone, however, does not give a positive proof of the formation of such structures and some other experiments would be necessary (e.g., NMR or HREM – high-resolution electron microscopy).

The porous structure described above is in agreement with the model consisting of nonparallel layers stacked under a certain angle to each other. Submicropores observed in such a structure are present at the part of the system where two layers either touch each other or are near to each other forming a "bottleneck".

XPS spectra show peaks of Si, Al and O with binding energies typical for montmorillonites [17] and that for Zr typical for Zr oxides [18]. The surface composition of the studied smectites is given for M1, M1Mn07 and M2 in table 4. From table 4 it may be seen that:

Table 4
Surface composition of the studied catalysts (O+Zr+Si+Al = 100 at%).

Sample	Surface content (at%)			
	O	Zr	Si	Al
M1	69.4	6.7	17.4	6.4
M1Mn07	69.1	6.8	17.1	7.0
M2	65.6	9.5	19.6	5.3

(i) The comparison of pillared clay either unpromoted or promoted with Mn (M1 and M1Mn07) shows that the surface ratio of Al/Si stays constant. The introduction of Mn does not influence this ratio.

(ii) Upon acid modification, the content of surface aluminium decreases considerably from Al/Si of 0.40–0.27 (cf. M1 and M2).

(iii) The surface content of Zr is higher for M2 than M1 (Zr/Si, respectively, 0.48 and 0.39). This effect may be connected with different distribution of ZrO_2 in the studied samples. As M2C contains lower bulk amount of zirconia than M1C, this would suggest that apart from the formation of pillars, some ZrO_2 precipitation is possible for M2 preferentially on the outer surface of smectite particles leading to higher XPS Zr/Si ratio. The fact that no separate phase was registered in XRD proves that thus precipitated zirconia is amorphous.

(iv) The lack of Mn 2p maximum (M1Mn07) indicates the depletion of the outer surface of the catalysts particles in Mn. Similar effects were observed for smectites either treated or untreated with acid and promoted with manganese from aqueous solutions containing saccharose [19], while the impregnating solutions without saccharose resulted in bigger aggregates of Mn oxides mostly on the outer surface of catalysts particles. Taking into account that textural changes after promotion with Mn are very small even for considerable amounts of introduced active material, it may be concluded that Mn is present in the form of small clusters and/or individual cations on the inner surface of the studied samples.

The overall structure of the catalysts may be therefore assumed to be formed by nonparallel layers of inorganic material. The HCl-treated samples are Al-depleted. There is obviously less carbon inside the porous system for acid-treated than untreated supports. This may be connected with the decrease in aluminium content, as the density of pillars is higher for the M1C than the M2C series (cf. bulk amounts versus XPS surface Zr/Si ratios). The effect would be due to the smaller amounts of anchoring sites for polymer introduced into the system. It was shown before [10] that the used polyacryloamide is sorbed on Al–OH sites of montmorillonite layers and not on pillars. The smectite used in this study is different from that described before [10], but it may be safely assumed that it should not influence the general mechanism of polymer interaction to a meaningful extent. Thus the depletion in Al sites for M2 could explain why less polymer is introduced into the system to form M2C, resulting in much lower micropore volume decrease than for M1C.

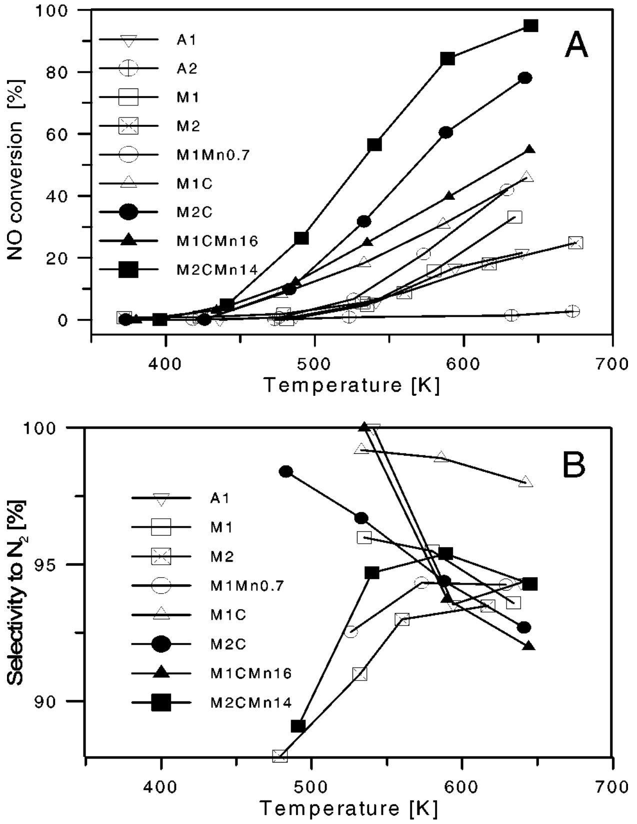


Figure 4. (A) Activity and (B) selectivity to N_2 of the catalysts under study.

3.2. Catalytic tests

Catalytic activity and selectivity to nitrogen for M1 and M2 series samples are shown in comparison to untreated montmorillonite A1 and HCl-treated A2 in figure 4 (A) and (B). Sample A2 was omitted in the selectivity diagram as it is catalytically inactive (cf. figure 4(A)). On similar grounds for all other samples selectivity was shown only for higher temperatures (from 473 K onwards). The activity forms the following sequence:

$$\mathrm{A2} < \mathrm{A1} \approx \mathrm{M2} < \mathrm{M1} < \mathrm{M1Mn07} < \mathrm{M1C} < \mathrm{M1CMn16} < \mathrm{M2C} < \mathrm{M2CMn14}.$$

From figure 4 (A) and (B) it may additionally be derived that:

(i) HCl-treated motmorillonite (A2) does not show any catalytic activity throughout the whole studied temperature range in contrast to A1, for which some NO conversion (up to ca. 20%) was observed at higher temperatures. The possible reason for this behaviour may be connected with changes in bulk composition upon HCl treatment, among others some decrease in Fe_2O_3 content (cf. table 2).

(ii) All preparation steps – pillaring, carbon deposit modification and manganese promotion – increase activity, cf.

$$\mathrm{M2} > \mathrm{A2};\ \mathrm{M2C} > \mathrm{M2};\ \mathrm{M2CMn} > \mathrm{M2C} \quad \text{or}$$

$$\mathrm{M1} > \mathrm{A1};\ \mathrm{M1Mn} > \mathrm{M1};\ \mathrm{M1C} > \mathrm{M1};\ \mathrm{M1CMn} > \mathrm{M1C}.$$

On the whole, however, M2 series catalysts are much more active than M1 series.

(iii) The samples of the M1 series without the addition of carbon do not show any catalytic activity at temperatures lower than 473 K. For the M2 series the activity curve is shifted to temperatures lower by ca. 50–100 K. Additionally, the introduction of carbon deposits somewhat decreases the onset temperature of the SCR reaction.

(iv) The selectivity to N_2 is within ca. 90–100% and decreases slightly with temperature for A1 and M1 while it increases for M2. The trends observed in selectivity show that the addition of carbon moderately decreases the production of N_2O (cf. A1, M1 versus M1C). The slightly lower selectivity to N_2 for M2C than for M1C is in good agreement with the assumption that there is less penetration with carbon for this support. Mn-containing catalysts behave for the M1 and M2 series in a different way (for M2CMn the selectivity increases and for M1CMn it decreases).

The produced amount of N_2O is, on the whole, very low in all cases, except for one experimental point at 493 K for M2CMn14 which, due to rather low overall production of N_2O and N_2, is measured with high error. It is in reasonable agreement with the behaviour of different supports (active carbon, carbon-covered smectites or smectites) with small clusters and/or individual cations of manganese deposited on the surface [5,19,20] which showed near to 100% selectivity up to 573 K. The difference may be explained by a somewhat lower sensitivity of detection of the products (gas chromatography, NDIR) than in this study. When catalysts containing small clusters are compared with supports with larger aggregates of manganese oxides on the outer surface [5,19,20] the role of the latter in the formation of N_2O becomes obvious.

Simultaneously it must be stated that it was observed for the mentioned catalysts that larger deposits of manganese oxides shift the maximum activity to a much lower temperature region (ca. 413 K) [5,19,20]. These differences in activity and selectivity between larger deposits and small clusters/individual cations lead to a speculation that the former catalyze the SCR reaction by a somewhat different mechanism (possibly via a dual site) than the latter (single site). However, a certain influence of diffusion for catalysts containing small Mn deposits over the whole surface cannot be neglected.

4. Conclusions

The modification of smectites with carbon and promotion with manganese results in active and selective catalysts.

The XRD studies show that there is no long-range ordering in the c-direction for calcined catalysts, possibly due to the formation of a delaminated structure.

The texture and the extent to which carbon deposits are introduced onto the inner surface depend on the pretreatment of the starting montmorillonite. When a pillared sample obtained from untreated smectite is contacted with polymer, more carbon deposits are formed inside the porous system than in the case of the use of smectite initially (before pillaring) pretreated with the solution of hydrochloric acid. The composition of the surface is also dependent on acidic pretreatment, which removes some aluminium from the structure.

Moreover, the initial acidic pretreament before pillaring influences the activity and selectivity in the SCR reaction. The modification with carbon increases the activity and somewhat improves the selectivity to N_2. The ex-acid treated samples are, however, more active than those based on untreated smectites. Due to lower amounts of carbon deposits inside the porous system the selectivity is slightly smaller for the former than for the latter catalysts. Overall selectivity is, however, quite good despite high amounts of introduced manganese which may be explained by its presence on the surface preferentially as small clusters and/or individual cations.

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