Selective catalytic reduction of nitric oxide with ammonia on Mn-promoted carbonized used silica–alumina sorbents

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Deactivated (waste) silica–alumina sorbents were carbonized and used as supports. The introduction of manganese led to active and selective SCR catalysts at low temperatures. Two methods of Mn promoting were compared: wet impregnation and adsorption. They influenced the distribution of Mn and N_2O production. The catalysts behaved similarly to Mn-promoted active carbon.

Keywords: selective catalytic reduction, nitric oxide, ammonia, Mn-promoted silica–alumina

1. Introduction

Selective catalytic reduction of nitric oxide with ammonia (SCR) is the reaction used on industrial scale for the cleaning of stack gases from stationary sources [1,2]. Many types of catalysts were proposed for this reaction, mainly oxide/hydroxides or salts of vanadium, chromium, copper, iron or manganese on traditional supports or active carbons [1,3–5]. The role of supports is not quite clear but it was observed that promoted active carbons exhibited high activity at much lower temperatures (ca. 423 K) than the same active materials introduced onto traditional inorganic supports [6]. This may lead to improvements in selectivity for the former catalysts as undesirable N_2O is produced in a side reaction at higher temperatures. On the other hand, active carbons are predominantly microporous; most of their surface area is hardly accessible in pores with diameter of ca. 0.7 nm. In this respect some inorganic supports with larger pores should be more advantageous than carbonaceous materials. In order to combine the good characteristics of both types of supports, inorganic substances containing a thin layer of carbon could be used. It was reported that such composite materials may be prepared from smectites by either polymerization of organic molecules *in situ* or adsorption of certain organic substances, such as polymers, and subsequent carbonization [7–9]. This opens also a possibility of using waste materials from organic industry, e.g., sorbents from separation or cleaning processes which were deactivated by chemisorption of organic molecules or their fragments. The reactivation of such materials would be costly and tedious and instead they could, after proper preparative steps, be used as supports containing “islands” or a thin layer of carbonaceous material on an inorganic base.

This report deals with the preparation of such materials from deactivated sorbents from the vegetable oil industry and their testing as supports for SCR catalysts.

2. Experimental

2.1. Preparation

Deactivated sorbents from the vegetable oil industry were carbonized at 773 K in nitrogen to form a support which was pelletized using 10% montmorillonite as binder (AK). The bulk composition of the support as determined by X-ray fluorescence is given in table 1 and elemental analysis (C, N and H) in table 2.

AK was promoted with manganese by wet impregnation from a methanol solution of manganese(II) nitrate(V) or by adsorption from an aqueous solution of the same compound and saccharose (Mn to saccharose weight ratio = 9.2). All samples were dried at 353 K for several hours. The preparation method and the amount of introduced manganese are summarized in table 3 together with specific surface areas, S_{BET}, calculated from the nitrogen sorption isotherm measured at 77.5 K by a volumetric method.

2.2. Characterization

The structure of the starting support AK was characterized by X-ray diffraction using a X-ray diffractometer Philips X’Pert and Cu K_α radiation.

The manganese distribution was determined by X-ray photoelectron spectroscopy. The spectra were recorded with a Leybold LH-10 spectrometer with a Mg K_α source and a multichannel plate analyzer working in FAT mode (AE = constant) at a 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 was better than 3×10^{-8} mbar. The spectra were smoothed, a nonlinear background was subtracted and the fitting was carried out with a convolution of 50/50 Lorentzian and Gaussian curves. The main C 1s peak was used as an internal standard to calibrate binding energies (284.6 eV) and the ele-

Table 1
The bulk composition of the support as determined by X-ray fluorescence (wt%).

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	LOI[a]
0.54	2.37	16.04	68.25	0.05	0.75	0.54	0.19	0.04	1.69	10.34

[a] LOI mass loss by fusion.

Table 2
The elemental analysis (C, N and H) of support AK.

	Element		
	Carbon	Hydrogen	Nitrogen
Content (wt%)	3.5	0.8	0.0

mental composition was calculated taking the area of the peaks and the sensitivity factors of Wagner et al. [10].

2.3. Catalytic tests

Catalytic activity and selectivity were studied in a fixed-bed reactor under the following conditions: mass of catalyst 500 mg; composition of the mixture: 800 ppm NO and NH_3, 3% O_2 in helium and a flow of 100 ml/min. The concentrations of educts and products (NO, N_2O and CO_2) were measured on-line using a NDIR spectrometer (Hartmann and Braun).

Before a catalytic experiment the samples were calcined on-line at 523 K for 2 h with a mixture of 3% O_2 in helium and a flow of 100 ml/min. The calcination was prompted by the work on manganese-promoted active carbons [5] which showed that calcined catalysts were both more active and more stable than noncalcined ones. During calcination decomposition of rest nitrate was observed.

As the support comes from an industrial process it may exhibit heterogeneous nature. This heterogeneity was distinctly presented in XRD experiments where the spectra which were repeated several times showed different intensities for some additions beside main phase (smectite). It may be also expected that the amount of carbon may not identical for supports prepared in this way. However, these differences proved not to be very important from the catalytic point of view. It was observed for two strongly different batches of the support (prepared separately) that the activity was within experimental error for all the temperatures except 573 K, where it somewhat exceeded experimental error (ca. ±3%), but the difference was not very significant.

For AK-A, as a representative of catalysts prepared by wet impregnation, and AK-E representing the second preparation method, internal diffusion tests were carried out. No effect was found in the first case while considerable diffusion limitation was observed in the second.

3. Results and discussion

3.1. Structure of the catalysts

The diffraction pattern of the main phase in the support was almost identical with a dioctahedral Na-smectite ($Na_x(AlMg)_2Si_4O_{10}(OH)_2\cdot zH_2O$) but the material of the support was very heterogeneous and contained additionally impurities such as quartz, feldspars, calcite and dolomite. Presence of graphite (from active carbon) and illite ($(KH_3O)Al_2Si_3Al_{10}(OH)_2$) was also recorded.

X-ray photoelectron spectroscopy showed Si, Al and O peaks at positions typical for montmorillonites [11]. The binding energy of Mn $2p_{3/2}$ was 642.2 ± 0.3 eV for all samples except AK-E where no manganese peak was detected. This is consistent with Mn^{3+} and/or Mn^{4+} [12–15]. There is no possibility of differentation in XPS between these two oxidation states other than the determination of the width of the Mn 3s splitting [15] but unfortunately in all cases the Mn 3s peak was too small. The composition of the studied samples is given in table 4. From the table it may be seen that:

(i) the comparison of Mn/C, Mn/Al or Mn/Si ratios showed considerable amounts of manganese on the surface which increased with the growing bulk Mn content for samples prepared by wet impregnation. For higher amounts, however, the relative increase was smaller than for lower ones, and

(ii) sample AK-E did not show any manganese on the outer surface.

The XPS results point to aggregates of manganese oxides formed mainly on the outer surface of the particles of the support for all the samples except AK-E, where an enrichment of the inner surface in manganese may be stated. Some active material was most probably introduced also into the porous system of catalysts prepared by wet impregnation (AK-A, AK-B, AK-C, AK-F and AK-G) in the form of deposits inside the pores or at the inlet to the pores. This may be proven firstly by the decrease in specific surface area. S_{BET} values (cf. table 1) form a sequence AK $>$ AK-C $>$ AK-F $\approx$ AK-B. AK-A had a specific surface area lower than the support but higher than AKB. This is more difficult to explain but we think that bigger manganese crystallites on the outer surface of the support may produce their own surface area. Similar effects we observed previously for manganese-promoted active carbons [16]. Secondly, the amount of manganese on the surface as given by XPS increased with the bulk amount of manganese although not linearly.

On the other hand, if we take into account that the change in specific surface area between the support and AK-E is within experimental error, it may be assumed that in this case only small clusters and/or individual cations of manganese are present inside the particles of the support

Table 3
The preparation method, the amount of introduced manganese and specific surface area for the catalysts under study.

	Sample						
	AK-A	AK-B	AK-C	AK-E	AK-F	AK-G	AK-H
Method of Mn introduction[a]	A	A	A	B	A	A	A
Mn content (wt%)	10.0	5.0	1.0	2.7	2.5	1.75	2.0
S_{BET}[b] (m^2/g)	85.2	61.4	85.0	97.2	60.3	[c]	[c]

[a] A – wet impregnation from methanol solution of manganese(II) nitrate(V). B – adsorption from aqueous solution of manganese(II) nitrate(V) and saccharose (Mn to saccharose weight ratio = 9.2).

[b] Specific surface area S_{BET} for the support AK 98.6 m^2/g.

[c] Not measured.

Table 4
The surface composition of the studied samples as given by XPS.

Sample	Mn content (wt%)	Mn/C (at%/at%)	Mn/Al (at%/at%)	Mn/Si (at%/at%)
AK-A	10.0	0.182	[a]	0.080
AK-B	5.0	0.158	0.230	0.080
AK-C	1.0	0.078	0.095	0.034
AK-E	2.7	[b]	0[b]	0[b]
AK-F	2.5	0.144	0.141	0.052
AK-H	2.0	0.138	0.111	0.042

[a] Not measured.

[b] Manganese peak was not registered for this sample.

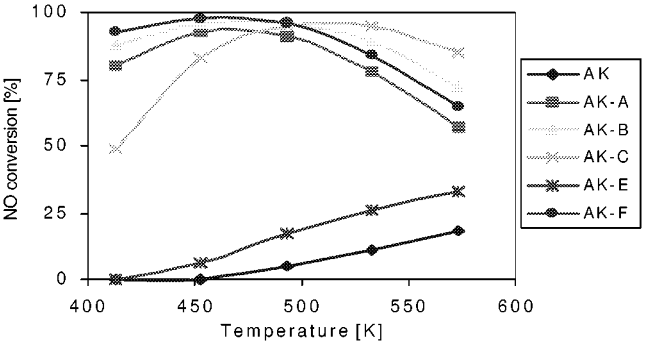

Figure 1. NO conversion for catalysts modified with Mn oxides.

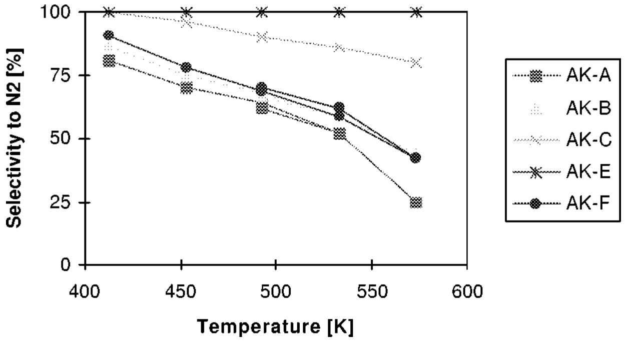

Figure 2. Selectivity to N_2 for catalysts modified with Mn oxides. Selectivity to N_2 for the support AK (not included in the figure) was 100% at all temperatures.

and no bigger deposits inside or at the inlet of the porous system are prevalent.

3.2. Catalytic performance

Figure 1 depicts activity of the support and the studied catalysts and figure 2 shows their selectivity to N_2. In order to make the pictures more clear samples AK-G and AK-H are not shown. The activity for AK-G at 413 K lay between that for AK-C and AK-A and other experimental points almost coincided with those for AK-F. Selectivity was, within experimental error, the same as for AK-F. AK-H had the same activity and selectivity (within experimental error) as AK-F.

From the pictures it may be seen that the support exhibited only small activity in the studied reaction. The comparison with typical active carbon is, however, difficult since some high ash materials showed high [3] while others low activity [5], possibly depending on the ash distribution. The addition of manganese increased conversion of NO to a degree depending on the introduction method of Mn and the amount of introduced Mn. The catalysts prepared by wet impregnation with a Mn content above 1.75 wt% Mn (AK-A, AK-B, AK-F and AK-H) are distinctly different from the sample prepared by adsorption from an aqueous solution of manganese nitrate containing saccharose (AK-E) and the samples with a low Mn content (1 or 1.75 wt% Mn, AK-C and AK-G). For the first group the activity was high, the selectivity to N_2, on the other hand, was good only at 413 K and decreased rapidly with temperature. For AK-E activity was low at 413 K and increased somewhat with temperature, while selectivity was 100% for all experimental points. Sample AK-C containing the lowest amount of Mn (introduced by wet impregnation) lay in-between, having at 413 K an activity twice higher than AK-E and twice lower that AK-F and selectivity 100% while at higher temperatures it was more similar to the catalysts prepared by wet impregnation. For sample AK-G the effect was smaller than for AK-C.

This division into two types of samples coincides well with XPS data showing large amounts of manganese on the outer surface of the grains of the AK support for the first group and some small amount inside the porous system and exclusively small clusters and/or individual cations of active material on the whole surface for AK-E. It may be suggested that the portion of the active material which was present inside the particles of the catalyst, was not totally accessible for the reaction, as suggested by internal diffusion tests. For lower bulk Mn contents, the portion of active material inside the porous system may lead to somewhat different behaviour for AK-C (and to less extent by AK-G) than for AK-A, AK-B or AK-F, especially at low temperatures, where diffusion effects play a greater role. At 413 K NO conversion for both samples is markedly lower than for other catalysts obtained by wet impregnation. At higher temperatures the reaction rate predominated over diffusional effects and the samples were more similar to AK-A–AK-F.

On the whole, activity versus temperature changed rather little for the studied catalysts and thus reminded more of the behaviour of active carbons [5] than of montmorillonites promoted with the same active material [16], where the dependence of NO conversion on temperature is concerned. The increased N_2O formation at higher temperatures was, however, mostly or perhaps exclusively influenced by the presence of large manganese crystallites and not by the type of the support. This was shown before for both active carbons promoted with Mn [5] and montmorillonites containing Mn [17]: small clusters led only to nitrogen as product in contrast to large crystallites (on the outer surface of the particles of the supports) which resulted in considerable amounts of dinitrogen oxide.

In order to check the possibility to improve the selectivity to N_2 by a second element, AK-B was additionally promoted with 1 wt% iron by wet impregnation using an aqueous solution iron(III) nitrate. Almost no influence on activity was found but the selectivity to N_2 improved by ca. 10% (absolute) at all experimental temperatures.

The stability of the catalysts was studied in the following way: calcination at 523 K in helium for 2 h, catalytic reaction at increasing temperatures (413, 453, 493, 533 and 573 K) for 90 min at each step and then at decreasing temperatures (533 and 493 K). No difference in NO conversion or selectivity was found for both (upward and downward) experimental curves.

Sample AK-F which showed good activity and selectivity to N_2 at low temperatures was additionally selected for a lifetime test carried out at 413 K for 50 h (figure 3). Both activity and selectivity stayed almost constant throughout the experiment.

Together with NO and N_2O, carbon dioxide production was monitored at the outlet of the reactor. The produced amounts of CO_2 both for the support and the catalysts were low (ca. 50–100 ppm at $T < 533$ K and ca. 200 ppm at 573 K) and could partly come from the decomposition of carbonates, which were found by XRD to be present in the samples. This allows the conclusion that no excessive gasification of the carbonaceous overlayer would lead to the changes in the structure of the support.

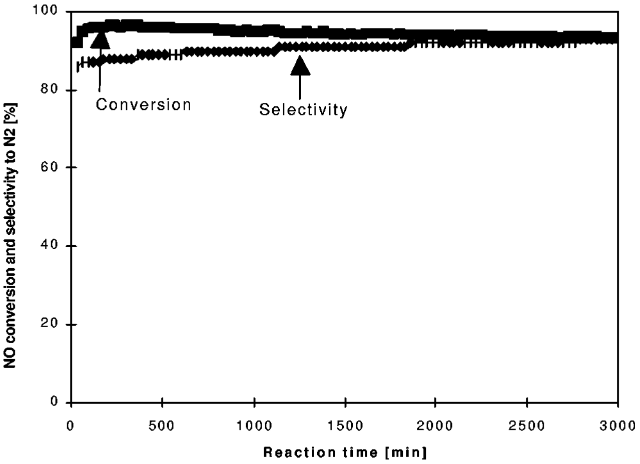

Figure 3. Lifetime test for catalyst AK-F at 413 K.

4. Conclusions

Deactivated (waste) silica–alumina sorbents may be used to prepare cheap supports for catalysts for selective catalytic reduction of NO with ammonia. The introduction of manganese leads to an active and selective SCR catalyst at low temperatures (413 K).

The catalytic behaviour of catalysts prepared in this way was similar to that of Mn-promoted active carbons. Activity and selectivity were influenced by the method of Mn introduction. Manganese introduced by wet impregnation was distributed in the form of larger crystallites, mostly on the outer surface of the particles of the support resulting in an increased production of N_2O at higher temperatures but at low temperature (413 K) selectivity to N_2 was good. Selectivity to N_2 could be improved by the addition of iron oxides. Catalysts were stable in the presence of oxygen at the temperature range of 413–573 K.

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