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Carbon-covered clays as catalytic supports. 1. Iron-promoted samples as denox catalysts

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Deactivated sorbents from the oil industry were carbonized and used as supports which after promotion with Fe oxides were tested in selective catalytic reaction (SCR). The catalysts were characterized by N_2 sorption, X-ray photoelectron spectroscopy and temperature-programmed desorption ammonia. Catalysts were active at a medium temperature range ($\sim$473–573 K). Selectivity to N_2 was 100%. Oxygen content influenced catalytic performance. H_2O led to reversible poisoning, while SO_2 addition to the SCR mixture resulted in irreversible poisoning.

KEY WORDS: SCR; montmorillonite; iron oxide; XPS.

1. Introduction

Natural clays have found extensive application as sorbents and catalysts in industry due to their numerous possibilities of structural, textural and/or chemical modification. It has been demonstrated recently that montmorillonite thus modified increased its activity as a catalyst in selective reduction of NO with ammonia (SCR) [1]. On the other hand, spent smectite sorbents in the oil industry are covered by carbon-containing molecules and/or their fragments, thus forming a waste which may be difficult and costly to dispose of.

The subject of this work was to study deactivated sorbents from the vegetable oil industry as supports for iron oxides/hydroxides as SCR catalysts. The choice of active material was prompted by several articles which showed that these species supported on clays, titania, alumina or active carbons [2–4] were active in SCR and did not produce dinitrogen oxide, an environmentally hazardous by-product of NO reduction.

2. Experimental

2.1. Preparation of catalysts

Waste sorbents from the vegetable oil industry were carbonized at 773 K in dinitrogen for 30 min, pelletized with the addition of 10 wt% montmorillonite as binder and again heated under the above-mentioned conditions, thus giving support AK. Bulk composition of the support and elemental analysis are given in tables 1 and 2 [5]. The support was subsequently promoted with Fe^{3+} by wet impregnation with an aqueous solution of iron(III) nitrate, giving samples AK1Fe, AK2.5Fe and AK5Fe, containing respectively 1, 2.5 or 5 wt% Fe.

2.2. Structure

For the obtained samples the following experiments were carried out.

1. Specific surface area and total pore volume by low temperature dinitrogen sorption using ASAP2000 (Micromeritics). Before each experiment samples were outgassed at 523 K for several hours.
2. Surface composition and oxidation degree of the elements by X-ray photoelectron spectroscopy using a Leybold LH-10 spectrometer equipped with an Mg K_α anode and a multichannel plate detector working in FAT mode ($\Delta E = \text{const}$) 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 Shirley background was subtracted and the fitting was carried out with a convolution of 50/50 Lorentzian and Gaussian curves. The Si 2p peak (103.1 eV) was used as an internal standard to calibrate binding energies. The content of elements was calculated taking the area of the main peaks (Al 2p, Si 2p, C 1s, Fe 2p, O 1s) and the sensitivity factors of Wagner *et al.* [6].
3. Acidity by temperature-programmed desorption of ammonia, carried out in the following way: before the experiments a sample (100 mg) was calcined at 673 K for 1 h at 25 ml/min of nitrogen, followed by cooling to 338 K. Then ammonia was sorbed at

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

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 upon heating at 1273 K.

338 K and the sample was flushed with helium (flow 25 ml/min) for 1 h in order to remove physically-adsorbed species. Desorption was carried out with a heating rate of 10 K/min in helium (flow 50 ml/min) up to 873 K. The following desorption products were registered by a mass spectrometer: NH_3 (mass No. 15), H_2O (18), CO (28), NO (30), and CO_2 (44) and SO_2 (64).

2.3. *Catalytic tests*

Catalytic activity and selectivity were studied in a fixed-bed microreactor under the following conditions: mass of catalyst 500 mg; composition of the reaction mixture: 800 ppm NO, 800 ppm NH_3, 3% O_2 in helium and a flow of 100 ml/min. Before reaction, samples were calcined at 523 K for 2 h in a mixture of 3% O_2 in helium and a flow of 100 ml/min. Educts and/or products (NO, N_2O, CO_2) were analyzed with an NDIR analyser (Hartmann and Braun). Additionally, the influence of oxygen concentration (0–10%, $T = 493$ K), water (0–10%, $T = 493$ and 533 K) and sulfur dioxide (210 ppm SO_2, $T = 493$ K) on NO conversion and selectivity to N_2 were studied.

3. Results and discussion

3.1. *Characterization of the catalysts*

The measured dinitrogen adsorption isotherms are of type II according to BET classification and exhibit a hysteresis loop. Specific surface area S_{BET} slightly increased for all Fe-promoted samples in comparison with the support (98.6, 101.6, 105.6 and 104.0 m^2/g for AK, AK1Fe, AK2.5Fe and AK5Fe, respectively). The total pore volume decreased almost linearly with the introduced amount of iron (0.185, 0.188, 0.174 and 0.144 cm^3/g for support and samples containing 1, 2.5 and 5% Fe, respectively). It may therefore be assumed that the introduced active material at least partly blocks the pores while at the same time forming some additional surface area. After SCR with the addition of SO_2 to the mixture, the specific surface area decreased for AK5Fe* to 97.1 m^2/g while the total pore volume was somewhat higher (0.157 cm^3/g) than for an unpoisoned sample.

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

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

The surface composition for the studied samples is summarized in table 3.

Binding energies of the studied peaks (calibrated to Si 2p for montmorillonites at 103.1 eV [7]) showed the following features:

1. The main C 1s position coincided well with either graphitic carbon or C–H species (aliphatic hydrocarbons, aromatic hydrocarbons) [8]. The peak, however, was rather broad and had a tail towards higher binding energies, similar to active carbons, suggesting that oxygenated C species were also present on the surface.
2. Fe $2p_{3/2}$ was registered at ~713.1 eV for fresh uncalcined samples before reaction and at 712.6 eV after SCR reaction with SO_2-containing mixture. The former peak is connected with iron(III) nitrate as the presence of the nitrate was confirmed by TPD of surface oxides. The unusually high binding energy of Fe 2p peaks (literature value for Fe^{3+} is 711.0 eV [9–11]) suggests double charging due to bigger crystallites of iron nitrate on the surface. The iron 2p peak for the sample after SCR reaction with SO_2 is most probably sulfate. No peak S 2p for bulk sulfate was observed, suggesting thin layers of SO_4^{2-} or its partial redistribution into the pores. The latter hypothesis may be backed by observations of Grzybek *et al.* [12], who showed that during the reaction of SO_2 removal from stack gases the distribution of nickel- or cobalt-promoted active carbons changed in this way. An additional argument would be the decrease in specific surface area observed for the AK5Fe after SCR reaction with the addition of SO_2.

Table 3
Surface composition for Fe-promoted AK catalysts (at%)

Sample	Al	Si	C	O	Fe	S
AK2.5Fe	7.5	22.7	5.0	64.0	0.9	–
AK5Fe	8.4	22.5	5.8	62.2	1.1	–
AK5Fe*[a]	8.3	24.2	3.5	63.1	1.0	–

[a] After reaction with a mixture of: 800 ppm NO, 800 ppm NH_3, 210 ppm SO_2 and 3% O_2 in He.

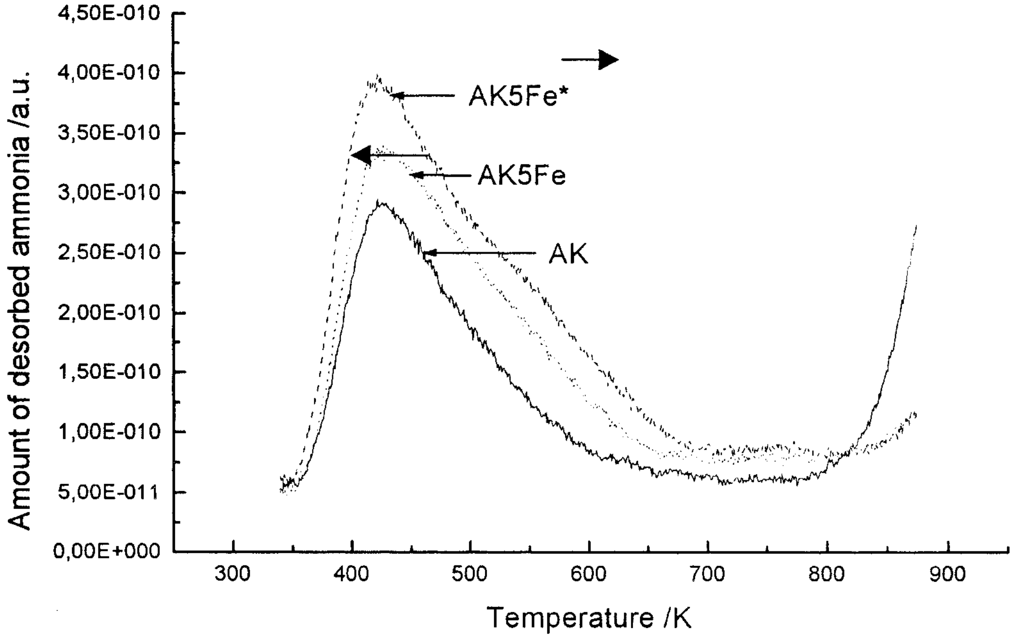

Figure 1. Temperature-programmed desorption of ammonia (mass No. 15) for AK, AK5Fe and AK5Fe* (after SCR reaction with SO_2 on-line).

From table 3 it may be seen that the amount of iron was high, again suggesting bigger crystallites with some iron present in the pores, as proven by the systematic decrease in total pore volume. In order to estimate the type of distribution, the intensity ratio of Fe 2p to C 1s was calculated according to the model of Kerkhof and Moulijn [13]. The calculated values are lower than experimental ones, which indicates some enrichment of the inner surface in active material and leads to crystallite sizes in porous systems roughly estimated to be ~4.5 and 7 nm, respectively, for AK2.5Fe and AK5Fe. Because after reaction with SO_2-containing mixture there was some change in the intensity ratio, the argument about the redistribution of active material under such reaction conditions seems to be validated.

Typical spectra of desorbed ammonia are compared in figure 1 for AK, AK5Fe and AK5Fe* (after SCR reaction with SO_2 on line). There is one broad peak for all samples with a long tail towards higher temperatures, proving that only relatively weak chemisorption sites for ammonia were present. The peak areas for mass No. 15 and the temperatures of maximum desorption are summarized in table 4. It may be seen that the addition of iron oxide to the support increased somewhat the number of sites for ammonia adsorption. The values depend on the amount of iron and form a sequence (the area $\times 10^8$ shown in parentheses):

$$\mathrm{AK}\,(3.3) \approx \mathrm{AK1Fe}\,(3.2) < \mathrm{AK2.5Fe}\,(4.2) \approx \mathrm{AK5Fe}\,(4.3)$$

A similar tendency was observed when promoting the support with manganese oxides. The increase was again not very high.

After treatment with SO_2-containing SCR mixture, additional new sites were formed. They are not identical with sulfate species because the desorption of mass No. 64 (SO_2) does not start before ~750 K.

3.2. Catalytic tests

NO conversion for the studied catalysts is shown in figure 2. The temperature-dependence of the NO conversion on AKFe catalysts is somewhat different from that for AKMn catalysts [5] and it is also steeper than in the case of iron-promoted active carbons [2]. Selectivity to N_2 was 100% at all studied temperatures. At lower temperatures (below 523 K) Mn-containing samples are more advantageous because their activity is higher and selectivity to nitrogen is reasonable since they produce only small amounts of dinitrogen oxide at this temperature. At medium SCR temperatures (from ~523 K) iron-containing catalysts showed comparable or higher activity than Mn samples and their selectivity to N_2 was 100% in

Table 4
Area of desorption peak (mass No. 15) and temperature of maximum desorption for the samples under study

Sample	Peak area $\times 10^8$/a.u.	Maximum temperature (K)
AK	3.5	424.6
AK[a]	3.2	425.8
AK1Fe	3.2	432.9
AK2.5Fe	4.2	420.8
AK5Fe	4.3	423.5
AK5Fe*[b]	5.3	420.4

[a] The measurement repeated for a new sample.
[b] See table 3.

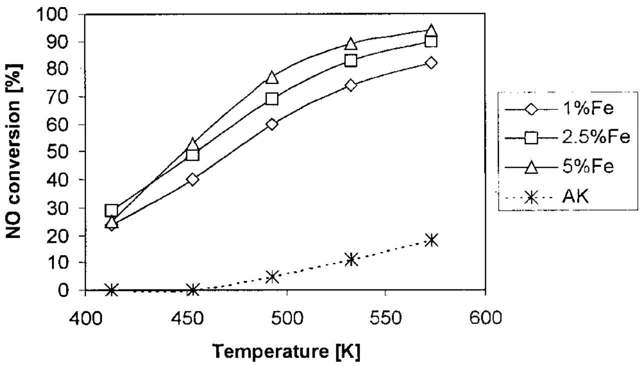

Figure 2. NO conversion as a function of temperature for catalysts AKFe in comparison with the support (AK).

comparison with considerable amounts of N_2O produced on AKMn 5.

The removal of oxygen from the reaction mixture resulted in a rapid decrease in NO conversion. The effect is reversible upon O_2 reintroduction. This phenomenon was observed for numerous catalysts, containing different active materials (*e.g.* [14]). What is, however, surprising is that the changes in O_2 content between 3 and 10% still led to a slight increase in NO conversion. The effect is more pronounced on AKFe than for a similar catalyst containing Mn (AKF, 2.5 wt% Mn) 5 where the NO conversion was different only by ~20 ppm, *i.e.*, practically within experimental error. Observations on the influence of oxygen amounts greatly exceeding stoichiometric values were also made for a reaction of SO_2 removal from stack gases, and it was speculated that there were two different reaction regimes for high and low oxygen contents, determining the kinetics of reaction—in both cases the rate-determining step was different [15].

The influence of water (0–10%) at 493 and 533 K on activity is shown in figure 3. It may be seen that H_2O led to reversible poisoning of the catalysts. The effect is possibly connected with competitive chemisorption of ammonia and water and was observed for numerous SCR catalysts (*e.g.* [16]).

The influence of SO_2 was studied for AK5Fe catalyst at 493 K in the following way: first NO conversion was measured for a mixture of 800 ppm NO, 800 ppm NH_3 and 3% O_2 in helium at 493 K for 3 h and subsequently 210 ppm of SO_2 were added to the reaction mixture. NO conversion as a function of reaction time for a mixture containing SO_2 is shown in figure 4. As may be seen from figure 4, NO conversion decreased rapidly upon SO_2 introduction up to about a third of its initial value. Most of the products were strongly bound on the surface. When the sample after reaction with SO_2 on line was heated in helium for 10 h at 493 K and then the SCR reaction (without the addition of SO_2) was repeated, there was only a slight improvement by ~8% of NO conversion. The TPD spectrum of the AKFe sample after reaction with an SO_2-containing mixture showed a SO_2 peak starting at ~750 K. This leads to speculation that the decrease in activity is mainly caused by the formation of iron sulfate, because $(NH_4)_2SO_4$ decomposes at 511 K and NH_4HSO_4 melts at 420 K and boils 623 K [17].

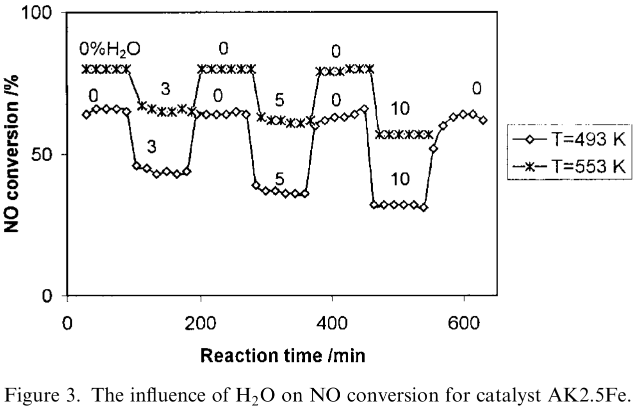

Figure 3. The influence of H_2O on NO conversion for catalyst AK2.5Fe.

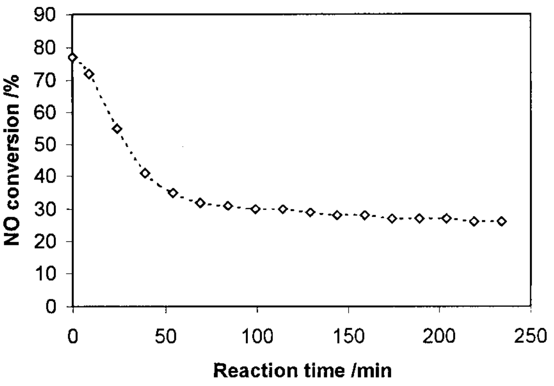

Figure 4. NO conversion as a function of reaction time for catalyst AK5Fe for a mixture of 800 ppm NO, 800 ppm NH_3, 3% O_2 and 210 ppm SO_2 in He at 493 K.

4. Conclusions

Deactivated sorbents after carbonization form a support which after promotion with Fe showed Fe^{3+} present on the surface. Before calcination it was in the form of nitrate. The active material was deposited partly on the outer surface of the particles of the support, but the model XPS calculations and systematic decrease in total pore volume as measured by sorption experiments led to the conclusion that some of it was also present inside the pores, in the form of crystallites (3–7 nm).

When used as SCR catalysts they were active at temperatures higher than for the Mn-promoted catalysts (493–533 K). Selectivity to N_2 was 100% at all temperatures. Catalysts were reversibly poisoned by H_2O at 533 and 573 K. The removal of O_2 from the reaction mixture led to a reversible decrease in NO conversion, while SO_2 poisoned the AKFe catalysts irreversibly by the formation of iron sulfate and its redistribution inside the catalyst particles.

Therefore it may be concluded that spent montmorillonite sorbents after carbonization and promotion with iron oxides are promising SCR catalysts which may be used in the SO_2-free atmosphere.

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