Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 114 (2006) 319–325

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective catalytic oxidation of ammonia into nitrogen over PCH modified with copper and iron species

L. Chmielarz [a,*], P. Kuśtrowski [a], M. Drozdek [a], R. Dziembaj [a], P. Cool [b], E.F. Vansant [b]

[a] *Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland*

[b] *University of Antwerp, Department of Chemistry, Laboratory of Inorganic Chemistry, Universiteitsplein 1, 2610 Wilrijk, Belgium*

Abstract

Porous clay heterostructures (PCH) obtained on the basis of the synthetic saponite was used as a catalytic support for the deposition of transition metal (Cu, Fe) oxides. Transition metal oxides were introduced into the parent as well as ammonia treated PCH support by the ion-exchange method. The obtained catalysts were characterized with respect to their textural parameters (BET), composition (EPMA), chemical nature of the introduced transition metal species (UV–vis–DRS) and surface acidity (NH_3-TPD, FTIR). The modified PCH materials were tested as catalysts for the selective oxidation of ammonia to nitrogen and water. The studied catalysts have shown a very high selectivity towards N_2, which did not drop below 90% in a large studied temperature range (150–550 °C). However, the Cu-containing samples were active at temperatures significantly lower than PCH modified with iron.

Keywords: Porous clay heterostructures; PCH; Selective catalytic oxidation; Ammonia; Copper; Iron

---

1. Introduction

The abatement of ammonia from industrial waste streams is becoming increasingly important due to environmental concerns. The selective catalytic oxidation (SCO) of ammonia into nitrogen and water seems to be the most promising method for the cleaning of large gas flows containing oxygen and low ammonia concentrations [1,2]. This method could be applied for the treatment of waste gases emitted in processes in which ammonia is used as a reactant or ammonia is produced as a by-product. On the other hand, ammonia is an effective reducing agent used in power plants for the NO_x abatement by the selective catalytic reduction ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$). The commercial catalysts used for this process are based on the V_2O_5–TiO_2 oxide system [3]. To control ammonia release, the majority of the $DeNO_x$ processes are carried out with the ratio of NH_3/NO below 1 (~0.9), which results in a decrease in efficiency of the NO_x conversion. The effectiveness of the NO_x reduction can be improved by the use of stoichiometric or even excess amount of ammonia. Afterwards, the residual ammonia could be selectively oxidized to N_2 and H_2O in a secondary catalyst bed [4]. Various types of materials have been studied as catalysts for the ammonia SCO process. Noble metals (e.g. Pt [5,6], Pd [5,7], Ir [8,9], Ru [7], Ag [8,9]) have been found to be very active catalysts for the ammonia oxidation which operate in the low temperature region. Unfortunately, ammonia is not only oxidized to nitrogen but also to nitrogen oxides. The next group of the studied catalysts for the ammonia SCO process is based on transition metal oxides (e.g. MnO_2, Co_3O_4, Fe_2O_3, CuO, MoO_3, V_2O_5 [10–17]). In general, these catalysts show higher selectivity to nitrogen but operate at temperatures significantly higher than noble metals. Zeolites modified with transition metals have been found to be promising catalysts for the selective oxidation of ammonia. Long and Yang showed a high activity of copper and iron deposited on the ZSM-5 [18] and Y [19] zeolites. A decrease in the Si/Al ratio improves the catalytic activity of zeolites. An additional increase in the activity of the Fe-modified zeolites can be obtained by deposition of noble metals (Pt, Pd, Rh) [20]. However, an introduction of these metals into the Fe-containing zeolites resulted in a decrease in the nitrogen selectivity.

Porous clay heterostructures (PCH) are a new group of porous materials which are characterized by combined micro- and mesoporous structure, a very large surface area, porosity and high thermal stability [21]. Due to these properties, PCHs

---

* Corresponding author. Tel.: +48 12 6632006; fax: +48 12 6340515.
E-mail address: chmielar@chemia.uj.edu.pl (L. Chmielarz).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.01.020

are very attractive materials for potential catalytic applications. The synthesis of the PCH materials consists of some steps [22]. Firstly, cationic templates and neutral amine co-templates are intercalated in the interlayer space of host clay forming micelle structures. Secondly, the silica pillars are created by in situ polymerization of silica source (e.g. TEOS) around them. Finally, the organic templates are removed from the material by a classical calcination producing a high surface area and porous material. The negative charge of the clay layers is compensated by protons formed during decomposition of the organic templates. These protons can be exchanged for other cations. Such modification of PCHs offers the possibility for an introduction of catalytically active components by a classical ion-exchange method.

2. Experimental

2.1. Catalysts preparation

Synthetic saponite (Kunimine Industries Co., Japan) characterized by the chemical formula of $(Na_{0.49}Mg_{0.14})^{+0.77}[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})(OH)_4O_{20}]^{-0.77}$ was used as a starting material for the PCH preparation. Parent clay was added to a solution of the surfactant (hexadecyltrimethylammonium chloride) and stirred at 50 °C for 24 h. Subsequently, the clay was separated from the solution and washed with demi-water till a pH of 7 was reached. In the next step, the modified clay was added to a neutral amine (dodecylamine) and a silica source (tetraethylorthosilicate, TEOS). The mixture was allowed to react for 4 h under continuous stirring. Then the modified clay was separated from the solution, dried at room temperature and finally calcined at 550 °C for 6 h to produce the PCH sample.

After calcination, a part of the obtained PCH was treated with ammonia in order to transform protons compensating the negative charges of the clay layers into NH_4^+ cations. The modification of PCH was performed in a flow reactor. The sample was outgassed at temperature 450 °C in a flow of pure helium for 2 h. Then, the temperature of the reactor was decreased to 200 °C and a flow of helium was exchanged for a flow of a gas mixture containing 1 vol.% of NH_3 diluted in He. The reactor outlet was directly connected to a QMS detector, which continuously measured the consumption of ammonia. When ammonia appeared in the outlet gases, a flow of the NH_3 containing mixture was switch off and the sample was purged in a flow of pure helium at a temperature of 200 °C for 2 h. The PCH pre-treated with ammonia is denoted as PCH-NH_3.

Transition metals (Cu and Fe) were introduced into the PCH support by the ion-exchange method using aqueous solutions (0.02 M) of $Cu(NO)_2{\cdot}H_2O$ or $Fe(NO_3)_3{\cdot}9H_2O$. The samples modified with copper and iron were dried in air at room temperature and then calcined in air at 450 °C for 3 h.

2.2. Catalysts characterization

Textural parameters of the samples were determined by N_2 sorption at −196 °C using a Quantachrome Autosorb-1-MP automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 200 °C for 16 h. The surface area was determined using the BET equation, while the micropore volumes of the samples were calculated using the t-method of DeBoer.

Transition metal loadings were determined by electron microprobe analysis performed on a JEOL JCXA 733 superprobe (electron probe microanalysis, EPMA).

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were recorded on a Nicolet 20SXB spectrometer for the samples (2 wt.%) diluted in KBr. Two hundred scans were taken with a resolution of 4 cm^{-1}.

The UV–vis–DRS spectra of the samples were recorded on a Nicolet Evolution 500 spectrophotometer. The measurements have been performed in the range of 200–900 nm with a resolution of 2 nm for the samples (2 wt.%) diluted in KBr.

Surface acidity of the samples was studied by temperature programmed desorption of ammonia (NH_3-TPD). The measurements were performed in a flow microreactor system equipped with a QMS detector (VG Quartz). Prior to the ammonia sorption, a sample was outgassed in a flow of pure helium at 450 °C for 1 h. Subsequently, the microreactor was cooled down to 70 °C and the sample was saturated in a flow of a gas mixture containing 1 vol.% of NH_3 in helium for about 30 min. Then, the catalyst was purged in a helium flow until a constant baseline level was attained. Desorption was carried out with a linear heating rate (10 °C/min) in a flow of pure helium (20 ml/min) or in a flow of a gas mixture containing 5 vol.% of O_2 in He (20 ml/min). Calibration of QMS was carried out with commercial mixtures allowing recalculating the detector signal into the rate of NH_3, N_2, NO, N_2O and NO_2 evolution.

The chemical nature of the acid sites was studied by FTIR measurements of the samples preadsorbed with pyridine. Transmission FTIR spectra were recorded using wafers in the form of self-supporting pellets of the catalyst powder. The pellet was placed in an IR cell equipped with KBr windows properly designed to carry out spectroscopic measurements at different temperatures. The cell was connected to a vacuum line allowing all thermal treatments and adsorption–desorption experiments to be carried out in situ. Prior to pyridine adsorption, the sample was outgassed overnight at 200 °C under vacuum. Then the cell was cooled to room temperature and the catalyst was allowed to react with pyridine for 1 h. FTIR spectra were recorded on a Nicolet 20SXB spectrometer after treatment the sample at temperature 180 °C under vacuum for about 2 h. Two hundred scans were taken with a resolution of 4 cm^{-1}.

2.3. Catalytic tests

The catalytic performance of the PCH based samples in the selective oxidation of ammonia has been studied under atmospheric pressure in a fixed-bed flow reactor (i.d., 7 mm; *l*, 240 mm). The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG Quartz) connected to the reactor via a heated line. Prior to the reaction,

Table 1
Texture parameters, transition metal loading and surface acidity of PCH based samples

Sample	S_{BET} (m^2/g)	$V_{\mathrm{tot.}}$ (cm^3/g)	V_{micro} (cm^3/g)	Transition metal content (wt.%)	NH_3 sorption (μmol NH_3/m^2)
PCH	903	0.743	0.602	–	0.022
PCH-NH_3	855	0.717	0.581	–	–
PCH-Cu	832	0.696	0.563	0.59 (Cu)	0.047
PCH-NH_3-Cu	800	0.675	0.539	1.43 (Cu)	0.137
PCH-Fe	840	0.702	0.560	1.43 (Fe)	0.053
PCH-NH_3-Fe	783	0.679	0.527	1.41 (Fe)	0.049

each sample of the catalyst (100 mg) was outgassed in a flow of pure helium at 450 °C for 1 h. The composition of the gas mixture at the reactor inlet was $[NH_3] = 0.5\%$, $[O_2] = 2.5\%$ and $[He] = 97\%$. Total flow rate of the reaction mixture was 40 ml/min, with a space velocity of about 12,000 h^{-1}. The reaction was studied at temperatures ranging from 50 to 550 °C. The intensities of the mass lines corresponding to all reactants and possible products were measured at a given temperature for at least 30 min after the reaction had reached a steady-state. The signal of the helium line served as the internal standard to compensate small fluctuations in the operating pressure. The sensitivity factors of the analyzed lines were calibrated using commercial mixtures of gases. The possible changes in a molar flow caused by the NH_3 conversion were negligible in the diluted reaction mixtures.

3. Results and discussion

Textural parameters, transition metal content and surface concentration of chemisorbed ammonia measured for the parent PCH and its modified forms are comparatively presented in Table 1. PCH is characterized by a very high surface area, which exceeds 900 m^2/g, and combined micro- and mesoporosity. The treatment of the parent PCH with ammonia resulted in a slight decrease in the surface area and porosity. Introduction of transition metals onto the support also decreased its textural parameters, however these changes are more significant. Effectiveness of the ion-exchange method, used for the introduction of transition metals, depends on the nature of the cations compensating the negative charge of the clay layers in the PCH support. In the ammonium form of PCH (PCH-NH_3), a significantly higher amount of copper was introduced than in the support not modified with ammonia. Such an effect was not observed for the Fe-containing samples.

Fig. 1 presents DRIFT spectra recorded for the parent and ammonia treated PCH samples. For the PCH-NH_3 sample an additional peak at about 1430 cm^{-1}, related to the presence of NH_4^+ appeared [22]. Therefore, it could be concluded that protons present in the parent PCH were converted into NH_4^+ cations during the treatment of the support with ammonia.

The chemical nature of transition metal species present on the PCH surface were studied by UV–vis–DR spectroscopy. The results obtained for the samples modified with copper are shown in Fig. 2. The original spectra recorded for the Cu-containing catalysts were fitted by three bands. The first maximum, present at about 260 nm, is related to charge-transfer between mononuclear Cu^{2+} ion and oxygen, whereas the maximum centred at around 360 nm can be ascribed to charge-transfer between Cu^{2+} and oxygen in oligonuclear $[Cu–O–Cu]_n$ species [23–25]. Moreover, the peak at about 510–530 nm can be attributed to the d–d transition of Cu with an octahedral environment in CuO [26,27]. Therefore, it could be concluded that copper introduced onto the PCH supports is present in three different forms: isolated Cu^{2+} cations, oligonuclear $[Cu–O–Cu]_n$ species and bulky clusters of CuO. The distribution of copper among these species was

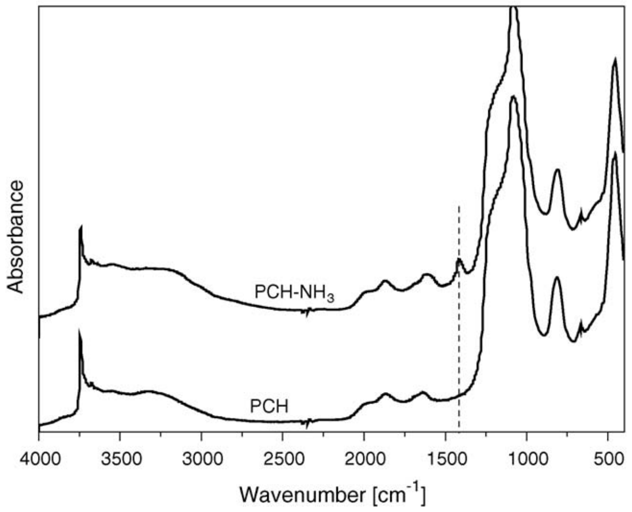

Fig. 1. DRIFT spectra of pure PCH and ammonia treated PCH.

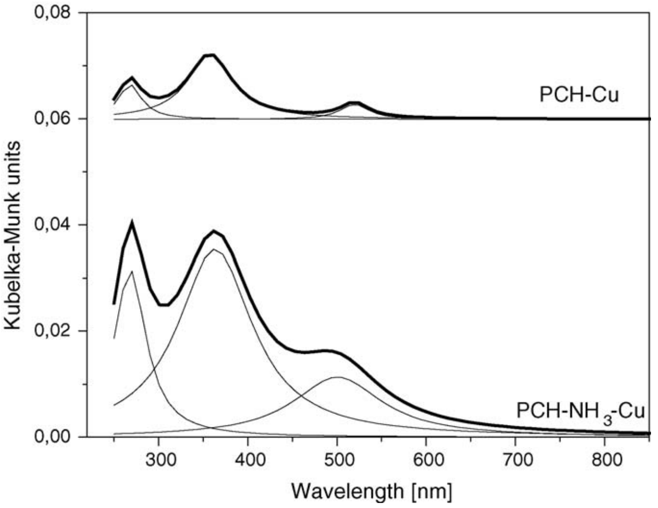

Fig. 2. UV–vis–DR spectra of Cu-containing samples.

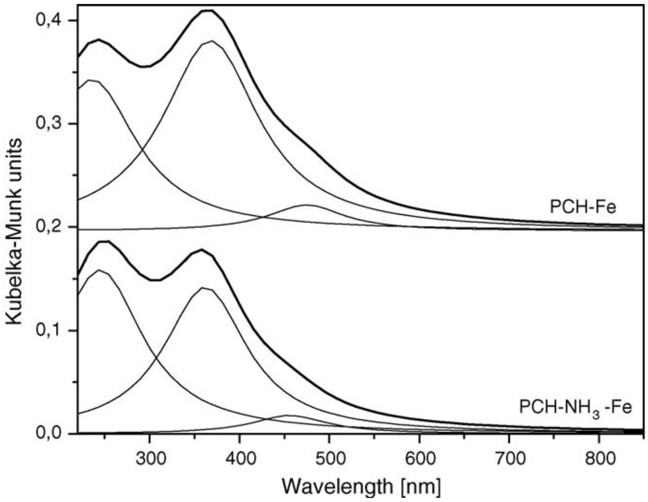

Fig. 3. UV–vis–DR spectra of Fe-containing samples.

determined on the basis of the areas of the deconvoluted peaks. For the PCH-Cu sample, about 20% of copper is present in the form of separated Cu^{2+} cations, 70% in oligomeric $[Cu–O–Cu]_n$ species and 10% in bulky CuO clusters. A slightly different distribution of copper species was found for the PCH-NH_3-Cu sample. About 22% of copper is present in the form of isolated Cu^{2+} cations, 57% in oligomeric $[Cu–O–Cu]_n$ species and 21% in bulky CuO clusters.

Three UV–vis–DR bands can be distinguished for the Fe-modified samples (Fig. 3). The peak, with a maximum centred at about 240 nm is related to isolated Fe^{3+} cations, while the second band, at about 360 nm corresponds to small oligonuclear $(FeO)_n$ species [28–30]. The small peak at 460–480 nm can be assigned to symmetrical and spin forbidden d–d transitions of Fe^{3+} [31]. Therefore, it could be concluded that iron deposited in PCH supports exists mainly in the form of isolated Fe^{3+} cations and oligonuclear $(FeO)_n$ species. The distribution of iron among these species is very similar for the both Fe-containing catalysts. In the case of PCH-Fe, about 58% of iron is present in the form of isolated Fe^{3+} cations and 42% in oligonuclear $(FeO)_n$ species, while for the PCH-NH_3-Fe sample distribution of Fe among these species is 54 and 46%, respectively.

The surface acidity of the samples was studied using the method of temperature programmed desorption of ammonia (NH_3-TPD). Surface concentrations of chemisorbed ammonia are presented in Table 1, while Fig. 4 shows desorption patterns obtained for the PCH samples. Parent PCH is characterized by a rather low surface acidity, which is represented by the surface concentration of chemisorbed ammonia of 0.022 μmol NH_3/m^2. In general, an introduction of transition metals into the PCH support resulted in a significant increase in its surface acidity. Therefore, it seems that transition metal species deposited on the support surface are responsible for the formation of additional centers for ammonia chemisorption. It should be noticed that the introduction of copper generates more sites for NH_3 chemisorption compared to the modification of PCH with iron.

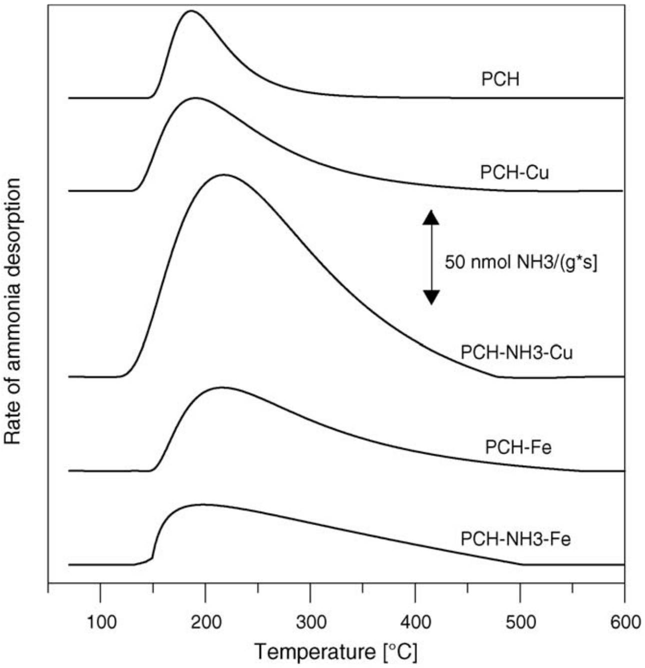

Fig. 4. Results of NH_3-TPD obtained for PCH based samples.

Ammonia desorption from the pure PCH sample (Fig. 4) is represented by an asymmetric maximum at about 200 °C. Desorption patterns obtained for the samples modified with transition metals are spread in the range from 140 to about 500 °C with maxima centered at 195–225 °C. It should be noticed that ammonia remains chemisorbed on these samples at temperatures significantly higher than on the pure PCH support. Therefore, it could be concluded that the introduced transition metals have a significant contribution in formation of stronger sites for ammonia chemisorption. The intensity of the desorption peak recorded for the PCH-NH_3-Cu catalyst is much higher than that obtained for PCH-Cu. These samples significantly differ in the Cu-loading, which is nearly three times higher for PCH-NH_3-Cu. Thus, these results prove that ammonia chemisorption sites are mainly located on the transition metal species dispersed on the support surface.

Fig. 5 shows the results of temperature programmed desorption of ammonia in a flow of gas mixture containing 5 vol.% of O_2 in He (NH_3-TPD–O_2). Apart from the ammonia desorption also evolution of products of its oxidation was detected. Nitrogen was the main product in the ammonia oxidation over the Cu-containing catalyst. A maximum N_2 formation was found at reaction temperatures between 200 and 420 °C. Small amount of chemisorbed ammonia was oxidized into N_2O at temperatures 300–430 °C over the PCH-Cu sample, while for PCH-NH_3-Cu a production of N_2O was detected in the range of 220–390 °C. The formation of small quantity of NO at temperatures 200–370 °C was additionally observed for this sample. These differences in the evolution of ammonia oxidation products, observed for the catalyst PCH-Cu and PCH-NH_3-Cu, could be explained by differences in transition metal loading as well as differences in the distribution of Cu-species on the support surface. The PCH-NH_3-Cu sample

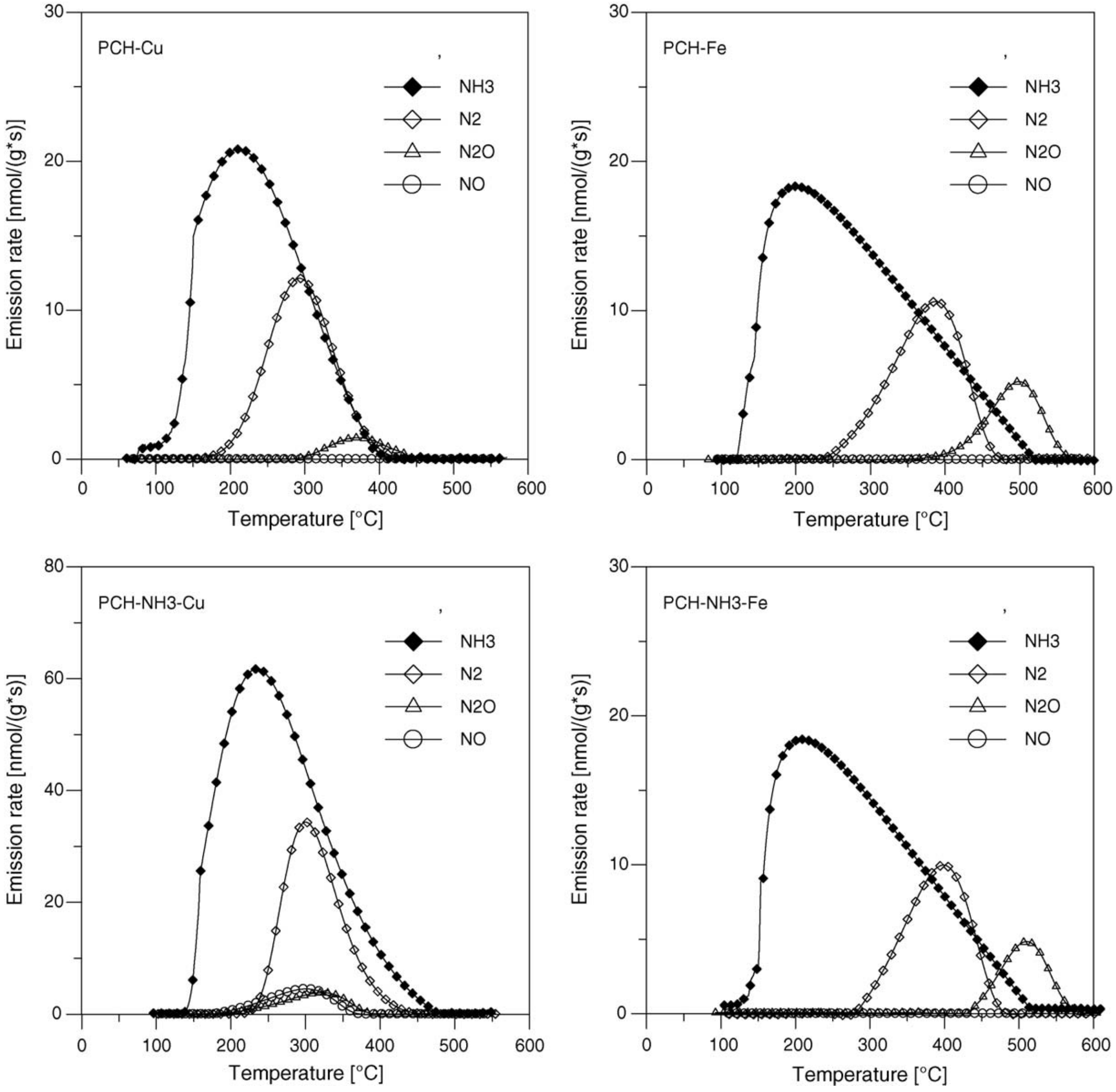

Fig. 5. Results of NH_3-TPD performed in flow of O_2/He gas mixture obtained for modified PCH samples.

contains a significant amount of copper in the form of bulky CuO oxide. Oxygen in such oxide is probably much weaker bounded than in the case of the other Cu-species present on the support surface [17]. Therefore, the oxidation of ammonia over PCH-NH_3-Cu was observed at lower temperature than for the PCH-Cu sample, which contains only very small quantities of copper in the form of bulky CuO clusters.

Ammonia chemisorbed on the Fe-containing catalysts was oxidized at temperatures above 240 °C. However, it should be noticed that the production of nitrogen occurred at significantly lower temperatures than that of N_2O. Therefore, it seems that ammonia strongly bonded into the catalyst surface is converted into N_2O, while ammonia molecules chemisorbed on weaker acid centers is oxidized mainly into N_2.

The chemical nature of acid sites was studied by pyridine adsorption. Fig. 6 presents the FTIR spectra of the PCH samples preadsorbed with pyridine. The spectrum recorded for the pure PCH material after the sorption of pyridine contains three well

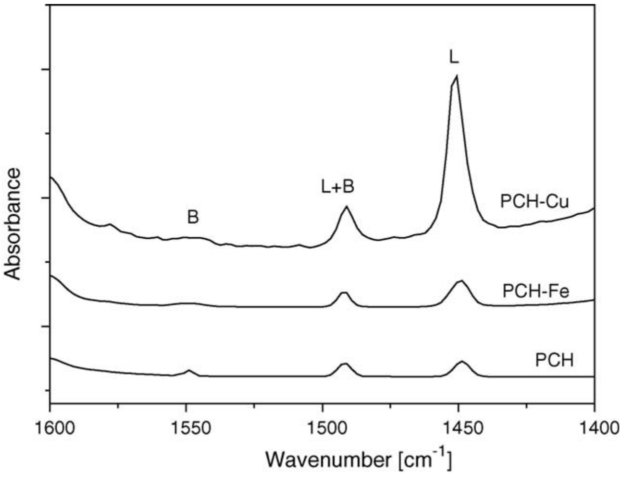

Fig. 6. FTIR spectra of the samples pretreated with pyridine.

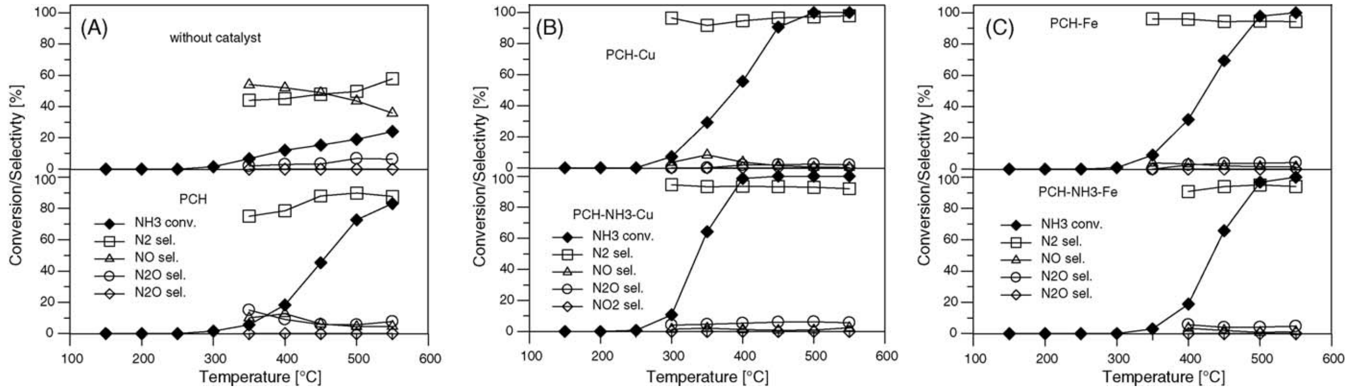

Fig. 7. Results of ammonia oxidation tests over PCH based catalysts.

resolved bands at about 1545, 1490 and 1450 cm^{-1} related to the chemisorbed forms of pyridine. The maxima at 1545 and 1450 cm^{-1} are attributed to pyridine adsorbed on the Brönsted and Lewis acid sites, respectively. While, the peak at about 1490 cm^{-1} is assigned to pyridine adsorbed on both Brönsted and Lewis acid centres. The Brönsted acidity can be related to the protons compensating negative charge of saponite layers. The Lewis acid sites exist in PCH, due to the presence of aluminium in the tetrahedral sheet of saponite clay. The modification of the PCH with transition metal ions resulted in an increase in concentration of the Lewis acid sites and a decrease in quantity of the Brönsted acid sites. This effect is probably related to the electron acceptors behaviour of the transition metal cations which give rise to additional Lewis acid centres. The reduction in Brönsted acid sites can be explained by replacement of protons by transition metal cations.

PCHs modified with transition metals were tested as catalysts of the selective oxidation of ammonia process. The desired products of this reaction are nitrogen and water vapor, while nitrogen oxides (N_2O, NO, NO_2) are side-products. Fig. 7A presents results of the catalytic tests performed in the absence of catalyst (gas phase) and in the presence of pure PCH. Oxidation of ammonia in the gas phase started at about 300 °C, however the NH_3 conversion did not exceed 25% at temperature below 550 °C. N_2 and NO are the main N-containing products of ammonia oxidation. Therefore, it could be concluded that the process performed in the gas phase is not selective. According to Stephens and Pease [32] the homogenous non-catalytic oxidation of ammonia proceeds via the chain radical mechanism. The significantly higher rate of NH_3 oxidation was obtained over the pure PCH support, however, it should be noticed that 100% of ammonia conversion was not measured in the studied temperature range. Nitrogen was detected as the main reaction product. Selectivity to NO and N_2O did not exceed 13 and 15%, respectively. Modification of the PCH support with transition metal oxides increased both its activity as well as selectivity to nitrogen. Fig. 7B shows the results of the catalytic tests performed for the Cu-containing samples. Oxidation of ammonia over these catalysts started at about 250 °C, and sharply increased with the temperature increase. For PCH-Cu, 100% of ammonia conversion was obtained at temperature 500 °C, while in the case of the PCH-NH_3-Cu catalyst, nearly total conversion of NH_3 was measured at 400 °C. These differences in the catalytic activity of the Cu-containing catalyst can be explained by differences in copper loadings (Table 1). For both the catalysts a very high selectivity towards nitrogen was observed, which did not drop below 92% in the whole studied temperature range. The Fe-containing samples have been found to be active at higher temperatures (Fig. 7C). Oxidation of ammonia over these catalysts starts at temperature about 300 °C and sharply increases with raising temperature. One hundred percent of ammonia conversion was obtained at a temperature of 550 °C. The selectivity to nitrogen is very high and did not drop below 94 and 91% for PCH-Fe and PCH-NH_3-Fe, respectively.

Copper and iron were studied as active components of various catalytic systems for selective oxidation of ammonia. Gang et al. [9] and Curtin et al. [14] have found high catalytic activity of CuO deposited on Al_2O_3. However, the selectivity to nitrogen obtained over the CuO/Al_2O_3 catalysts was significantly lower than that measured for PCHs modified with copper. Also mixed metal oxides (Cu–Al–Mg–O) obtained by calcinations of hydrotalcite materials have been found to be significantly less selective comparing to the PCH based catalysts [17]. Among the Fe-containing catalysts of the NH_3-SCO process, the most interesting seems to be modified zeolites. Long and Yang [7,12] have reported high activity of the Fe-modified zeolites with a relatively high selectivity to N_2. The catalytic performance of the catalysts depended mainly on the type of zeolite used for deposition of iron as well as the Si/Al ratio. The activity and selectivity obtained over the Fe-modified PCHs is similar to those reported for the most active zeolite catalysts. Therefore, it could be concluded that PCH materials modified with copper and iron are very promising catalysts for the NH_3-SCO process.

4. Conclusions

PCH material was obtained by a surfactant-directed assembly of silica species in the interlayer species of synthetic saponite. Part of parent PCH was pretreated with ammonia in order to convert protons compensating negative charge of saponite layers into NH_4^+ cations. Transition metals were introduced into pure as well as ammonia treated PCHs by an ion-exchange method. The Cu-loading in the sample modified with NH_3 was significantly higher than the quantity of copper introduced into parent PCH. Such an effect was not observed for the Fe-containing samples. Transition metals deposited on the PCH supports were present in the form of various species. For the copper containing catalysts, isolated Cu^{2+} cations, oligonuclear [Cu–O–Cu] species and bulky CuO clusters were identified. Iron deposited on PCHs was present mainly in the form of isolated Fe^{3+} cation and oligonuclear $(FeO)_n$ species. Distribution of transition metals in these species is slightly different for the supports treated and non-treated with ammonia. Transition metal oxides introduced onto the PCH support increased the surface acidity of the samples mainly due to formation of the Lewis acid sites. Nitrogen was the main product of oxidation of ammonia chemisorbed on the samples modified with transition metals. However, the production of N_2 from the Cu-containing catalyst occurred at temperatures significantly lower in comparison with the samples modified with iron. Only a small amount of chemisorbed ammonia was oxidized to N_2O and NO (detected only for PCH-NH_3-Cu). The PCH supports modified with transition metals have been found to be the active catalysts of selective oxidation of ammonia. The Cu-containing samples, especially the catalyst with higher loadings, operated in a significantly lower temperature range than PCHs modified with iron. The selectivity to nitrogen obtained over the studied catalysts was very high and did not drop below 90% in the whole studied temperature range.

Acknowledgments

The authors thank the Ministry of Flanders and the Polish Ministry of Scientific Research and Information Technology for financial support in the frame of bilateral Flemish–Polish project for 2004–2005.

References

[1] G. Olofsson, A. Hinz, A. Anderson, Chem. Eng. Sci. 59 (2004) 4113.
[2] Y. Li, J.N. Armor, Appl. Catal. B 13 (1997) 131.
[3] H. Bosch, F. Jansen, Catal. Today 2 (1988) 369.
[4] M. Amblard, R. Burch, B.W.L. Southward, Appl. Catal. B 22 (1999) L59.
[5] N.I. Il'chenko, Russ. Chem. Rev. 45 (1976) 1119.
[6] P.D. Sobczyk, E.J.M. Hensen, A.M. de Jong, A.S. van Santen, Top. Catal. 23 (2003) 109.
[7] R.Q. Long, R.T. Yang, Catal. Lett. 78 (2002) 353.
[8] J.J. Ostermaier, J.R. Katzer, W.H. Manoque, J. Catal. 41 (1976) 227.
[9] L. Gang, B.G. Anderson, J. van Grondelle, R.A. van Santen, W.J.H. van Gennip, J.W. Niemantsverdriet, P.J. Kooyman, A. Knoester, H.H. Brongersma, J. Catal. 206 (2002) 60.
[10] N. Il'chenko, G.I. Golodets, J. Catal. 39 (1976) 57.
[11] G.I. Golodets, Heterogenous Catalytic Reactions Involving Molecular Oxygen. Studies in Surface Science and Catalysis, Elsevier, Amsterdam, 1983.
[12] R.Q. Long, R.T. Yang, J. Catal. 207 (2002) 158.
[13] P. Fabrizioli, T. Burgi, A. Baiker, J. Catal. 206 (2002) 143.
[14] T. Curtin, F. O'Regan, C. Deconinck, N. Knutte, B.H. Hodnett, Catal. Today 55 (2000) 189.
[15] A. Wollner, E. Lange, H. Knozinger, Appl. Catal. A 94 (1993) 181.
[16] L. Lietti, G. Ramirez, G. Busca, F. Bregani, P. Forzatti, Catal. Today 61 (2000) 187.
[17] L. Chmielarz, P. Kuśtrowski, A. Rafalska-Łasocha, R. Dziembaj, Appl. Catal. B 58 (2005) 235.
[18] R.Q. Long, R.T. Yang, Chem. Commun. (2000) 1651.
[19] R.Q. Long, R.T. Yang, J. Catal. 201 (2001) 145.
[20] R.Q. Long, R.T. Yang, Catal. Lett. 78 (2002) 353.
[21] A. Galarneau, A. Barodawalla, T.J. Pinnavaia, Nature 374 (1995) 529.
[22] M. Benjelloun, P. Cool, T. Linssen, E.F. Vansant, Micropor. Mesopor. Mater. 49 (2001) 83.
[23] F.M.T. Mendes, M. Schmal, Appl. Catal. A 151 (1997) 393.
[24] M. Ramakrishna Prasad, G. Kamalakar, S.J. Kulkarni, K.V. Raghavan, J. Mol. Catal. A 180 (2002) 109.
[25] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki, F. Ohashi, J. Catal. 194 (2000) 373.
[26] M. Shimokawabe, H. Asakawa, N. Takezawa, Appl. Catal. 59 (1990) 45.
[27] G. Centi, S. Perathoner, D. Biglino, E. Giamello, J. Catal. 151 (1995) 75.
[28] M.V. Landau, E. Dafa, M.L. Kaliya, T. Sen, M. Hereskowitz, Micropor. Mesopor. Mater. 49 (2001) 65.
[29] M.A. Wojtowicz, J.R. Pels, J.A. Moulijn, Fuel Proc. Technol. 34 (1993) 1.
[30] R.A. Reimer, S.C. Slaten, M. Seapan, M.W. Lower, P.E. Tomlinson, Environ. Progr. 13 (1994) 134.
[31] E. Suzuki, K. Nakashiro, Y. Ono, Chem. Lett. 953 (1988).
[32] E.R. Stephens, R.N. Pease, J. Am. Chem. Soc. 72 (1933) 1187.