Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 242–246

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Vermiculites intercalated with Al_2O_3 pillars and modified with transition metals as catalysts of DeNO*x* process

L. Chmielarz [a,*], P. Kuśtrowski [a], M. Michalik [b], B. Dudek [a],
Z. Piwowarska [a], R. Dziembaj [a]

[a] *Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland*
[b] *Jagiellonian University, Institute of Geological Sciences, Oleandry 2a, 30-063 Kraków, Poland*

Abstract

Vermiculites intercalated with alumina pillars and modified with transition metals (Cu, Fe) were studied as catalysts of selective reduction of NO with ammonia. Prior to the pillaring process, a raw vermiculite was treated with a solution of nitric acid and then citric or oxalic acid in order to reduce the overall charge of layers. This modification was necessary for a successful pillaring of the clay. Transition metals (Fe, Cu) were deposited on the surface of the modified vermiculites by an ion-exchange method. The obtained samples were characterized with respect to composition (EPMA), structure (XRD), texture (BET) and chemical nature of deposited transition metal species (UV–vis–DRS). The vermiculite based materials have been found to be active and selective catalysts of the DeNO*x* process. The Cu-containing samples were catalytically active at lower temperatures than the pillared clays modified with iron. A side reaction of ammonia oxidation by oxygen decreased the effectiveness of the DeNO*x* process in the high temperature range.

Keywords: Pillared vermiculites; Al_2O_3; DeNO*x*; NH_3; Iron; Copper

1. Introduction

Pillaring of smectites via an exchange of interlayer cations with hydroxymetal polycations (e.g. Keggin-like Al_{13} species), followed by a thermal treatment, is an effective way for the preparation of high surface area microporous materials, which can be used in the role of adsorbents, catalysts and catalytic supports. The pillared smectites, especially montmorillonites, have been intensively studied as catalysts of various processes [e.g. 1]. Montmorillonites intercalated with Al_2O_3, TiO_2 or ZrO_2 and additionally modified with transition metals (e.g. Cu, Fe) were found to be active and selective catalysts of the DeNO*x* process [2–4]. Unfortunately, the pillared montmorillonites are characterized by a limited thermal stability resulting in a collapse of their structure at temperatures above 450–500 °C. Recently, del Rey-Perez-Calabero and Poncelet [5] have reported that significantly more stable microporous materials can be obtained by pillaring of natural vermiculites with alumina. The pillared structure of these clays is stable up to temperature as high as 800 °C. Direct intercalation of vermiculite is impossible due to a very high potential of stabilization of interlayer cations. This potential can be reduced by a partial leaching of Al^{3+} cations from the tetrahedral sheets of vermiculite in acidic medium. The extra framework aluminum ions are removed using complexing acids, and then the clay is converted to the sodium form by ion exchange. The charge-reduced vermiculite can be easily intercalated with alumina.

In the paper, the synthesis of microporous materials based on natural vermiculite as well as the study of their catalytic performance in the DeNO*x* process are presented.

2. Experimental

2.1. Catalysts preparation

Natural vermiculite, supplied by S&B Industrial Minerals GmbH, was used as a raw material for the preparation of the DeNO*x* catalysts. The starting clay was characterized by a low surface area (2 m^2/g) and total pore volume (0.004 cm^3/g). The

---

* Corresponding author.
E-mail address: chmielar@chemia.uj.edu.pl (L. Chmielarz).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.09.009

Table 1
Modifications of vermiculites and their textural parameters

Sample	Treatment with HNO_3	Treatment with complexing agent	Pillaring with Al_2O_3	Deposited metal	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)
Verm	–	–	–	–	2	2	0.002	0.002
V	+	–	+	–	123	170	0.115	0.070
V-Cu	+	–	+	Cu (1.1%)	114	160	0.106	0.063
V-Fe	+	–	+	Fe (5.1%)	103	147	0.096	0.052
VC	+	Citric acid	+	–	170	233	0.136	0.059
VC-Cu	+	Citric acid	+	Cu (0.8%)	161	221	0.126	0.054
VC-Fe	+	Citric acid	+	Fe (5.7%)	152	209	0.114	0.048
VS	+	Oxalic acid	+	–	203	275	0.153	0.076
VS-Cu	+	Oxalic acid	+	Cu (1.0%)	193	264	0.142	0.069
VS-Fe	+	Oxalic acid	+	Fe (5.7%)	170	234	0.134	0.060
Mt-Cu			+	Cu (0.4%)	138	185	0.105	0.073

modification of the vermiculite has been performed according to the procedure proposed by del Rey-Perez-Caballero and Poncelet [5]. This procedure consisted of the following steps:

Step 1: The raw clay material was leached with 10 ml of 0.8 M nitric acid solution per gram of vermiculite at 95 °C for 4 h under stirring. Then, the modified clay was washed, separated by filtration and oven dried.

Step 2: The acid treated clay sample was calcined at 600 °C for 4 h in static air.

Step 3: The calcined vermiculite was treated with oxalic acid or citric acid (10 ml of 0.12 M acid solution per gram of sample) at 80 °C for 3 h. Then, the resulting solids were washed, separated by filtration and oven dried.

Step 4: The materials obtained in step 3 were exchanged with a solution of NaCl (3 M). The slurry of 5 wt.% of the clay material was kept at 95 °C under stirring. This procedure was repeated four times. Then, the solid was washed and oven dried.

Step 5: The modified clay samples were pillared with aluminium oligocations. The pillaring solution was prepared by a slow addition of 0.1 M NaOH into $AlCl_3$ solution under constant stirring until the molar ratio of OH/Al reached 2.4. The solution was aged at room temperature for 2 weeks. Subsequently, the pillaring solution was slowly added into the suspension containing 1 wt.% of the sodium exchanged clay in deionised water until the Al/clay ratio reached the value of 10 mmol Al/g clay. The mixture was allowed to react at room temperature for 24 h. Then, the modified vermiculites were separated by filtration, washed with distillated water until chloride ions were removed and dried at 120 °C for 12 h. Finally, the samples were calcined at 500 °C for 12 h.

In the next step of the catalysts preparation, transition metals (Cu or Fe) were deposited on the Al_2O_3-pillared clays by an ion-exchange method using aqueous solutions (0.02 M) of $Cu(NO_3)_2\cdot 3H_2O$ or $Fe(NO_3)_3\cdot 9H_2O$. Then, the samples were dried at room temperature and finally calcined at 450 °C for 3 h.

The alumina-pillared montmorillonite modified with copper (Mt-Cu) was used as a reference sample. A detailed description of its preparation and characterization was presented previously [3].

The samples codes and method used for their preparations are presented in Table 1.

2.2. Catalysts characterization

Textural parameters of the samples were determined by N_2 sorption at −196 °C using an ASAP 2010 (Micromeritic) automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 350 °C for 12 h. The surface area was determined using the BET and Langmuir equations, while the micropore volumes of the samples were calculated using the t-plot method of DeBoer. The X-ray diffraction patterns of the samples were obtained with a Philips X'Pert APD diffractometer. Transition metal loadings in the clay samples were determined by electron probe microanalysis (EPMA) performed on a JEOL JCXA 733. The UV–vis–DR spectra of the samples were recorded on an Evolution 600 (Thermo) spectrophotometer. The measurements have been performed in the range of 200–900 nm with a resolution of 2 nm.

2.3. Catalytic tests

The modified vermiculites were tested as catalysts of the selective reduction of NO by ammonia. The catalytic experiments have been performed under atmospheric pressure in a fixed-bed flow microreactor. The outlet gases were analyzed by a mass spectrometer (VG-Quartz). Prior to the catalytic test each sample of the catalyst (100 mg) was outgassed in a flow of pure helium at 400 °C for 1 h. The catalytic tests were performed in the range of 100–500 °C using temperature steps every 50 °C. The same catalyst samples were tested at different temperatures. The composition of gas mixture at the reactor inlet was $[NO] = [NH_3] = 0.25$ vol.%, $[O_2] = 2.50$ vol. %. Helium was used as a balancing gas at a total flow rate of 40 ml/min. The intensities of the mass lines corresponding to all reactants and possible products were measured at a given temperature at least for 30 min after the reaction had reached a steady-state. The signal of the helium line served as an internal standard to compensate possible small fluctuations of the operating pressure.

3. Results and discussion

The textural parameters of the raw and modified vermiculites are presented in Table 1. The intercalation of the clay with alumina pillars increased its surface area and pore volume by about two orders of magnitude. The modified vermiculites are characterized by the presence of micropores, however also significant contribution of larger pores has been found. It should be noticed that the surface area and total pore volume of the VC and VS samples are significantly larger compared to the V sample. Therefore, it seems that the treatment of the samples with oxalic or citric acid is a very important step of the catalysts synthesis, which significantly improves their textural parameters. An introduction of transition metals into the Al_2O_3-pillared vermiculites slightly decreased their surface area and pore volume.

XRD patterns recorded for the raw vermiculite (Verm) as well as this clay intercalated with alumina (V, VC, VS) are shown in Fig. 1. The raw vermiculite exhibited two diffraction lines at about 7.1° and 8.9° indicating a presence of various cations (Mg^{2+}, Ca^{2+}) in the interlayer space of clay. The intercalation of vermiculite with Al_2O_3 pillars (sample V) resulted in a disappearance of peak at 7.1° and a decrease in an intensity of maximum at 8.9°. Additionally, a new peak at about 5.1°, related to vermiculite intercalated with Al_2O_3 has appeared. Therefore, it could be assumed that pillaring of vermiculite caused an increase in basal spacing from about 10 to 17.5 Å. It should be noticed that only fraction of vermiculite was successfully pillared with alumina. Significantly higher effectiveness of the intercalation process has been found for the samples treated with oxalic (VS) and citric acids (VC). The broad reflection observed in the diffractograms of the VS and VC samples at about 6.7° suggests that apart from Al_{13}-type species also smaller alumina aggregates were deposited in the interlayer space of vermiculite.

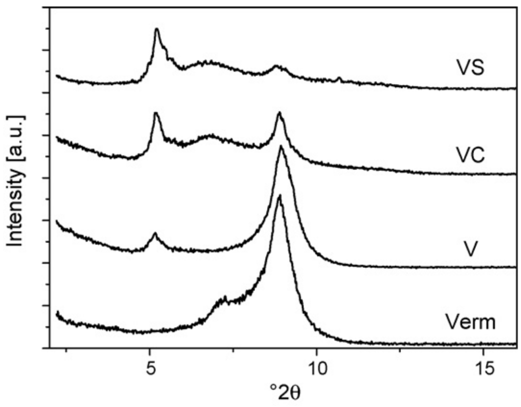

Fig. 1. XRD patterns of raw and alumina-pillared vermiculites.

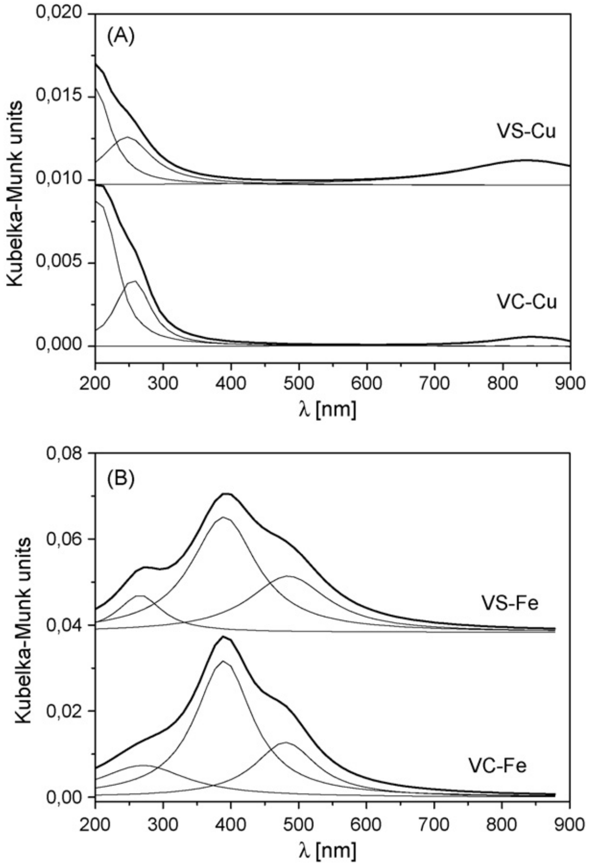

Fig. 2. Differential UV–vis–DR spectra recorded for pillared vermiculites modified with copper (A) and iron (B).

The chemical nature of transition metals deposited on the surface of Al_2O_3-pillared vermiculites was studied using UV–vis–DR spectroscopy. The differential spectra (the spectrum recorded for the support was subtracted from the spectra of the sample modified with transition metal) were recalculated into Kubelka–Munk units (Fig. 2). Such modification of spectra is necessary for their quantitative analysis. The spectra obtained for the Cu-containing samples were fitted by three bands (Fig. 2A). The first maximum, present at about 210 nm, is related to charge-transfer between mononuclear Cu^{2+} ion and oxygen, whereas the maximum centred at around 260 nm can be ascribed to charge-transfer between Cu^{2+} and oxygen in oligonuclear $[Cu–O–Cu]_n$ species [6]. Moreover, the peak at about 840 nm can be attributed to the d–d transition of Cu with an octahedral environment in CuO [7]. Therefore, it could be concluded that copper introduced onto the modified vermiculites is present in three different forms: isolated Cu^{2+} cations, oligonuclear $[Cu–O–Cu]_n$ species and bulky clusters of CuO. It should be noticed that the VS-Cu sample contains more copper in the form of CuO clusters and less in the form of isolated Cu^{2+} cations compared to VC-Cu.

Three UV–vis–DR bands can be distinguished in the spectra of the Fe-modified samples (Fig. 2B). The peak with a maximum centred at about 260 nm is related to the presence of isolated Fe^{3+} cations, while the second band at about 390 nm corresponds to small oligonuclear $(FeO)_n$ species [8]. The peak at 480 nm can be assigned to symmetrical and spin forbidden d–d transitions of Fe^{3+} [9]. Therefore, it could be concluded that iron deposited on the modified vermiculites exists mainly in the form of oligonuclear $(FeO)_n$ species and bulky Fe_2O_3 crystallites.

The modified vermiculites were tested as catalysts of the selective reduction of NO with ammonia. The results of these studies are presented in Fig. 3. The conversion of NO in the

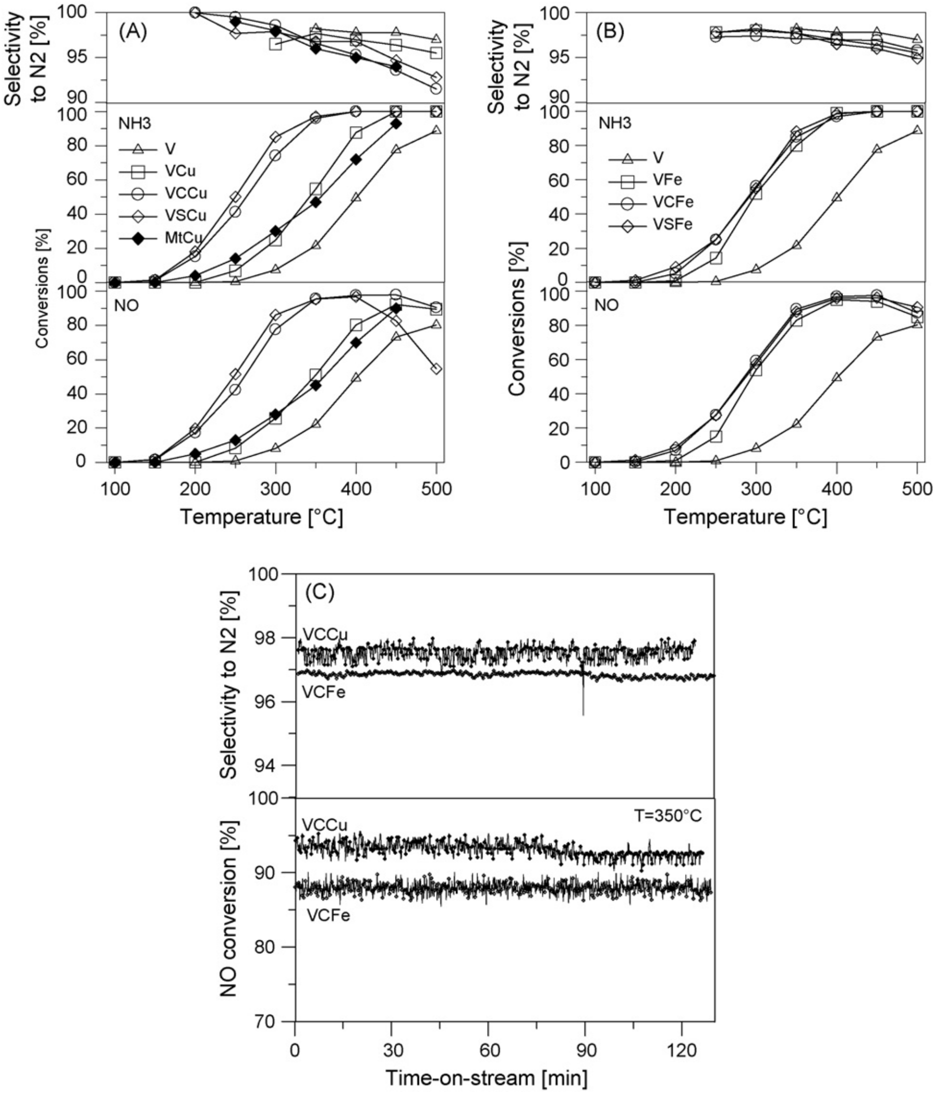

Fig. 3. Results of catalytic tests for Al_2O_3-pillared clays modified with copper (A) or iron (B) and stability tests (C) for VC-Cu and VC-Fe samples.

presence of the pillared vermiculite unmodified with transition metals (sample V) started at temperature 250 °C and increased to about 80% at 500 °C. Deposition of transition metals significantly increased the activity of the modified vermiculites. In a series of the Cu-containing samples the best catalytic results have been found for VS-Cu and VC-Cu, which were significantly more active than V–Cu as well as the reference Mt–Cu sample (Fig. 3A). For the most active catalysts, especially VS-Cu, a decrease of NO conversion in the high temperature region was observed. This effect is related to competitive oxidation of ammonia by oxygen present in the reaction mixture. It seems that bulky CuO clusters, which were found in significant larger amount in the VS-Cu sample compared to VC-Cu, are catalytically active in the low temperature DeNO*x* and additionally are responsible for ammonia oxidation at higher temperatures. Other Cu-species (isolated Cu cations and oligomeric copper oxide) are probably less active in the low temperature DeNO*x* but also are less active in ammonia oxidation. The kind of the catalytic support is an another factor significantly influencing the activity of the catalyst. Among the Cu-containing catalyst, alumina-pillared montmorillonite (Mt-Cu) was found to be less active than vermiculites intercalated with alumina (VS-Cu, VC-Cu). This effect could be related to differences in the surface acidity, textural parameters and natural impurities present in parent clays. The Fe-containing catalysts effectively catalyzed NO conversion at higher temperatures than the samples modified with copper (Fig. 3B). However, for this series of catalysts the side reaction of ammonia oxidation only slightly decreased the NO conversion in the high temperature range. For all the studied catalysts, the selectivity to nitrogen did not drop below 90% at temperatures lower than 500 °C. The results of stability studies are shown in Fig. 3C. It should be noticed that any significant changes in activity and selectivity was not observed for the studied catalysts during this experiment.

4. Conclusions

Transformation of vermiculite into high surface area microporous materials consisted of few steps. Prior to the pillaring process, vermiculite was treated with a solution of HNO_3 in order to reduce the overall negative charge of framework. Aluminum cations leached from the clay layers into the interlayer space of vermiculite were complexated by oxalic or citric acid. It was found that this step is necessary for an improvement of the effectiveness of the pillaring process. Intercalation of vermiculite with alumina pillars resulted in an increase of their surface area and pore volume by about two orders of magnitude. Transition metals (Cu, Fe) introduced into alumina-pillared vermiculites were present in the form of isolated cations as well as oligomeric and bulky metal oxide species. Isolated Cu^{2+} cations dominated in the case of the Cu-containing samples, while iron was present mainly in the form of oligomeric $(FeO)_n$ species. Alumina-pillared vermiculites modified with transition metals have been found to be very active, selective and stable catalysts of the DeNO*x* process. The samples modified with copper were more catalytically active at lower temperatures than the Fe-containing catalysts. In the high temperature range a decrease in the NO conversion caused by a side reaction of ammonia oxidation by oxygen was observed.

Acknowledgements

Authors acknowledge the Polish Ministry of Science for financial support in the frame of project PBZ-KBN-116/T09/2004 and S&B Industrial Minerals GmbH for supplying of natural vermiculite.

References

[1] P. Solerno, S. Mendioroz, Appl. Clay Sci. 22 (2002) 115.
[2] A. Vaccari, Catal. Today 41 (1998) 53.
[3] L. Chmielarz, P. Kuśtrowski, M. Zbroja, A. Rafalska-Łasocha, B. Dudek, R. Dziembaj, Appl. Catal. B 45 (2003) 103.
[4] L. Chmielarz, P. Kuśtrowski, M. Zbroja, W. Łasocha, R. Dziembaj, Catal. Today 90 (2004) 43.
[5] F.J. del Rey-Perez-Caballero, G. Poncelet, Micropor. Mesopor. Mater. 37 (2000) 313.
[6] F.M.T. Mendes, M. Schmal, Appl. Catal. A 151 (1997) 393.
[7] G. Centi, S. Perathoner, D. Biglino, E. Giamello, J. Catal. 151 (1995) 75.
[8] R.A. Reimer, S.C. Slaten, M. Seapan, M.W. Lower, P.E. Tomlinson, Environ. Progr. 13 (1994) 134.
[9] E. Suzuki, K. Nakashiro, Y. Ono, Chem. Lett. 953 (1988).