Journal of Thermal Analysis and Calorimetry, Vol. 77 (2004) 115–123

PILLARED MONTMORILLONITES MODIFIED WITH SILVER
Temperature programmed desorption studies

L. Chmielarz[*], *M. Zbroja, P. Kuśtrowski, B. Dudek,*
A. Rafalska-Łasocha and R. Dziembaj

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

Abstract

Alumina, zirconia and titania pillared montmorillonites additionally modified with silver were tested as catalysts of NO reduction with NH_3 or C_2H_4. Ammonia was much more effective reducer of NO than ethylene. The silver containing TiO_2-pillared clay has been found to be the most active catalyst for NO reduction both with NH_3 or C_2H_4. Oxidation of the reducing agents by oxygen limited the NO conversion in the high temperature region. The ammonia and nitric oxide adsorption sites were studied by the temperature programmed desorption methods (TPD).

Keywords: ammonia, DeNOx, ethylene, pillared montmorillonites, TPD

Introduction

Montmorillonite is a natural clay characterized by a laminar structure in which the negative charge of layers is compensated by interlayer cations (e.g. Na^+, Ca^{2+}) [1, 2]. Pillared clays are obtained by replacement of these common cations by large polynuclear cationic species, which during thermal treatment are transformed into metal oxide pillars. Such modification of montmorillonite increases its microporosity and surface area. The texture parameters can be controlled by the choice of a suitable pillaring agent. The density and strength of acidic surface centers might be increased by the acid-pretreatment of the clay materials, while the redox centers can be generated through the introduction of transition metals into the montmorillonite structure. The pillared clays are thermally stable up to about 400–500°C. Due to such properties, montmorillonites intercalated with metal oxides were found to be very interesting materials for catalytic applications [3–6].

Pillared clays modified with different transition metals were recognized as very promising catalysts for NO reduction due to their high activity and stability in the presence of typical components of flue gases (e.g. SO_2, water vapor) [7, 8]. This paper is concerned with the study of the alumina, zirconia and titania pillared montmorillonites additionally modified with silver as catalysts of NO reduction by ammonia or ethylene.

---

[*] Author for correspondence: E-mail: chmielar@chemia.uj.edu.pl

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The montmorillonite used in this study was the sodium-exchanged Wyoming bentonite (A-15). The cation exchange capacity of this clay is 83 meq per 100 g (the total charge of interlayer cations which compensates negative charge of the montmorillonite layers related to 100 grams of a dry clay material).

Alumina pillars were introduced to the montmorillonite by the ion-exchange method using an aluminium hydroxy-oligomeric solution. The pillaring solution was obtained by adding 0.1 mol NaOH into an $AlCl_3$ solution until the molar ratio of OH/Al=2.5 was reached. The modified montmorillonite was separated, washed with distilled water to remove chloride ions and then dried (120°C/12 h).

The solution of the titania oligocations was prepared by adding $TiCl_4$ into HCl until the final concentrations of Ti^{4+} and HCl equal to 0.82 and 0.11 mol, respectively were reached. The pillaring agent was then added to the montmorillonite suspension until the Ti/clay ratio reached a value of 10 mmol g^{-1}. The final product was separated, washed and dried at 120°C for 12 h.

The montmorillonite was pillared with zirconia using an aqueous solution of zirconyl chloride (10 mmol Zr/1 g of clay). The modified clay was separated, washed with distilled water to remove Cl^- ions and then dried (120°C/12 h). A more detailed description of the preparation procedure of the pillared montmorillonites was presented in a previous paper [9].

Silver was introduced into the pillared clays by the ion exchange method. One gram of the pillared montmorillonite was added to 100 mL of the 0.02 mol silver nitrate solution. The vigorously stirred suspension of the pillared clays was left in contact with the solution of transition metal nitrate at 60°C for 12 h. The silver modified clays were separated, washed and dried at 120°C for 12 h and then calcined at 400°C for 12 h.

The chemical composition of the samples was determined by X-ray fluorescence (XRF) using an Oxford 2000 instrument. The analytic response was calibrated using standard materials. The X-ray diffraction studies of the calcined montmorillonites were performed with a PW3710 Philips X'pert diffractometer using CuK_α radiation (λ=0.154178 nm). The BET measurements were performed using an ASAP 2010 instrument (Micromeritics). Prior to N_2 adsorption at liquid nitrogen temperature (–196°C), the samples of calcined clay were outgassed at 350°C under vacuum for 12 h.

The temperature-programmed desorptions of NH_3 (NH_3-TPD) or NO (NO-TPD) were carried out in the temperature range of 70–600°C in a fix bed continuous flow microreactor. The desorption temperature was measured with a K-type thermocouple located in a quartz capillary immersed in the catalyst bed. The molecules desorbing from the samples were monitored on-line by a quadrupole mass spectrometer (VG Quartz) connected to the reactor outlet via a heated line. Prior to TPD experiments, the clay sample (50 mg) was outgassed at 400°C for 1 h in a flow of helium (20 ml min^{-1}). Subsequently, the sample was cooled down to 70°C and saturated for about 30 min in a flow of 1% NH_3/He or 1% NO/He (20 ml min^{-1}). Then the catalyst was purged in a helium stream until a constant baseline was attained. Desorption was carried out with a linear heating rate (β=10°C min^{-1}) in a flow of He (20 ml min^{-1}). Calibration of the quadrupole mass spectrometer with commercial mixtures was performed to recalculate the detector signal into a desorption rate.

The activity of the modified clays as catalysts of NO reduction by ammonia was studied in a fixed-bed flow reactor. The reactant concentrations in the outlet stream were continuously measured using a quadrupole mass spectrometer (VG Quartz) connected on-line to the reactor. Prior to the reaction, each sample (200 mg, particle diameter 125–180 μm) was outgassed in pure helium at 400°C for 30 min. The composition of the gas mixture at the reactor inlet was $[NO]=[NH_3]=0.25\%$, $[O_2]=2.5\%$. Helium was used as a carrier gas at a total flow rate of 40 ml min^{-1}. The intensities of the mass lines corresponding to all reactants and 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. The sensitivity factors of analysed lines were calibrated using commercial mixtures of the gases. The possible changes in the molar flow caused by NO conversion were negligible in the diluted reaction mixtures.

A similar experimental system was used for testing the clay materials as catalysts of NO reduction with ethylene. However, in this case a gas chromatograph (Varian 3400 SX) was used for the outlet gases detection. GC was equipped with two packed columns (Porapak Q and Molecular Sieves 5A) and a TCD detector. Prior to the catalytic test the samples (200 mg, particle diameter 125–180 μm) were outgassed (400°C/30 min) in a flow of helium. The reactant mixture of 0.25% NO, 0.25% C_2H_4, 2.5% O_2 and 97% He entered to the reactor with a total flow rate of 40 ml min^{-1}.

Results and discussion

Table 1 presents the chemical composition and surface areas of the modified montmorillonites. Apart from the metals listed in this table, water and small amounts (below 1 wt. %) of Na_2O, K_2O, MgO were also detected. The modification of the pillared clays with $AgNO_3$ solution resulted in introduction of a very large amount of silver. The transition metal content was significantly higher than its quantity necessary for the compensation of negative charge of the montmorillonite layers. Thus, it seems that silver is deposited in the form of oxide clusters, which are thermally reduced during calcination.

Figure 1 presents the XRD patterns recorded for the raw montmorillonite and its modifications. Position of the (001) peak, which allows to determine the interlayer distance, for the clays pillared with alumina and zirconia was shifted to lower values of 2θ angle. The obtained results show that pillaring of montmorillonite with Al_2O_3 resulted in an increase of the interlayer distance from 0.32 to 0.96 nm, while in the case of the ZrO_2-intercalated clay the interlayer spacing increased to 1.19 nm. A disappearance of the (001) peak after pillaring of the parent montmorillonite with TiO_2 suggests that the obtained material is characterized by a delaminated structure (non parallel ordering of the clay layers). The broad peak at about 26° can be attributed to

Table 1. The chemical composition and surface areas of modified montmorillonites

Sample	Composition/mass %						S_{BET}/ m^2 g^{-1}
	Al_2O_3	SiO_2	TiO_2	ZrO_2	Fe_2O_3	Ag_2O	
Mt-Na	16.84	63.50	0.73	0.00	10.42	0.00	38
Mt-Al	23.25	58.51	0.47	0.00	6.72	0.00	254
Mt-Al-Ag	13.25	33.34	0.11	0.00	3.81	38.61	151
Mt-Ti	6.17	28.32	51.79	0.00	1.29	0.00	279
Mt-Ti-Ag	4.27	19.52	35.73	0.00	0.86	26.55	210
Mt-Zr	8.30	47.20	0.16	31.25	4.90	0.00	242
Mt-Zr-Ag	4.26	24.03	0.09	15.95	2.47	44.82	156

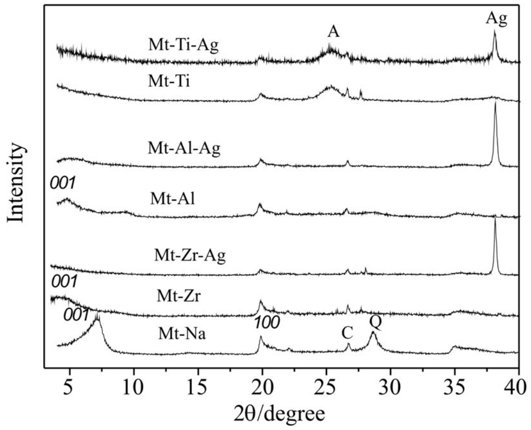

Fig. 1 X-ray diffraction patterns of montmorillonite and its modifications. Q-quartz, C-crystobalite, A-anatase, Ag-metallic silver

the presence of anatase (A), which was formed by a thermal decomposition of the pillaring agent deposited on the montmorillonite surface.

Modification of the pillared clays with Ag^+ cations results in an appearance of a new peak at about 38°, which is assigned to the presence of metallic silver. During the ion-exchange procedure, silver was deposited in the clay material in the form of separate cations and metal oxide clusters, which were thermally reduced to metallic silver (Ag) during the calcination process. A disappearance of the (001) peak, observed in the case of the Mt-Zr-Ag sample, suggests that silver clusters are localized partially in the interlayer space. Probably, these metal particles, which have various sizes, disturb ordering of montmorillonite layers.

The maxima at 26° and 28°, distinctly seen in the diffractogram of the parent clay, are attributed to the presence of the crystobalite (C) and quartz (Q) impurities.

The intercalation of the parent montmorillonite with metal oxide pillars resulted in a significant increase in its surface area nearly by an order of magnitude (Table 1) mainly due to the increase of microporosity of the pillared materials. The modification of the pillared clays with silver lowered their surface area by about 40% for Mt-Al, by 25% for Mt-Ti and by 35% for Mt-Zr. This might be explained by the blocking of interlayers with silver clusters.

The pillared clays modified with silver were tested as catalysts for reduction of NO by ethylene or ammonia. Figure 2 shows the results of catalytic studies performed with C_2H_4 as a reductant over the pillared montmorillonites doped with silver. Nitrogen was the only detected N-containing product. For all the studied catalysts, the reaction begins at a temperature of about 100°C. In the case of the Mt-Al-Ag and Mt-Zr-Ag samples, the NO conversion slowly increases to 10–14% at about 250°C. At higher temperatures, very small changes in the reaction rate were only detected. The Mt-Ti-Ag clay has been found to be much more active. Below 250°C, the NO conversion measured over this catalyst was very similar to those detected for the Mt-Al-Ag and Mt-Zr-Ag samples. However, in the range of 250–400°C a sharp increase in the NO conversion up to 60% was observed. For all the studied catalysts, the ethylene conversion was significantly higher than the conversion of NO, especially at higher temperatures. Thus, it should be concluded that ethylene does not react selectively with NO but is also oxidized by oxygen present in the inlet stream. This undesired process dominates at higher temperatures. It should be noticed that the NO conversion by ethylene over the pillared clays non-modified with silver did not exceed 5% in the whole studied temperature range (not shown).

The results of catalytic tests performed with NH_3 as a reductant of NO are presented in Fig. 3. N_2 and H_2O are desired products, while N_2O is an undesired one.

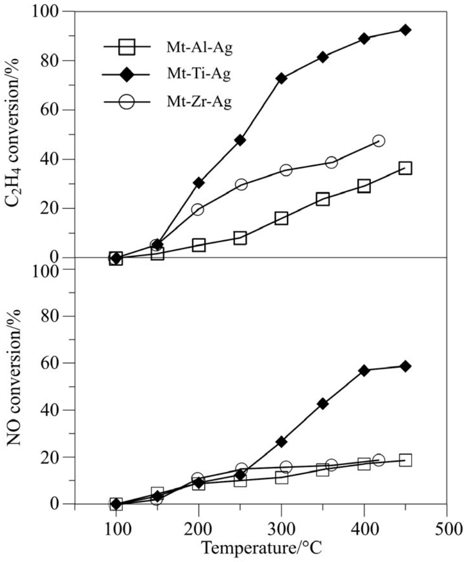

Fig. 2 Results of catalytic tests obtained for modified montmorillonites in reduction of NO by ethylene

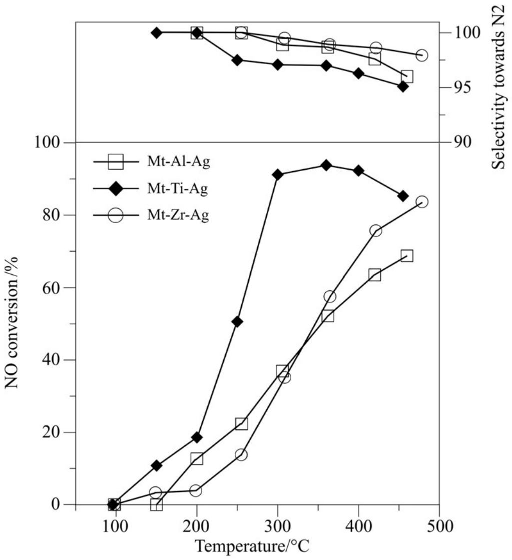

Fig. 3 Results of catalytic tests obtained for modified montmorillonites in reduction of NO by ammonia

Formation of any other gases was not detected. The modification of the pillared clays with silver drastically increased their catalytic activity. The results of catalytic tests performed over the pillared montmorillonites non-modified with transition metals were presented in our previous paper [9]. The obtained results indicate clearly that ammonia is much more effective reducing agent than ethylene. Among the studied samples, the Mt-Ti-Ag catalyst was found to be the most active one. The NO conversion that occurred over this catalyst exceeded 90% in the range of 280–400°C. At higher temperatures, the reaction rate decreased due to the competitive oxidation of ammonia by oxygen. The NO conversion over Mt-Al-Ag begins at about 150°C and increases to 70% at 470°C. In the low temperature region (T<300°C) the Mt-Zr-Ag sample was found to be the least active. However, at higher temperatures its activity significantly exceeded that measured for the Mt-Al-Ag sample. For all the studied catalysts, the selectivity to nitrogen is very high and does not drop below 95%.

The temperature programmed desorptions of NH_3 (NH_3-TPD) and NO (NO-TPD) have been performed in order to recognize the reaction mechanism. Figure 4 shows the results of NH_3-TPD experiments. Ammonia desorption pattern recorded for the Mt-Al-Ag sample is spread in the range of 140–550°C and consists of at least two unresolved maxima centered at about 220 and 400°C. The shape of the desorption spectra is typical for NH_3-TPD patterns of the alumina pillared montmorillonite [10]. Thus, it seems that chemisorption of ammonia takes place mainly on the surface of montmorillonite layers and alumina clusters. Introduction of silver into the titania pillared montmorillonite produced a new kind of surface acidic centers,

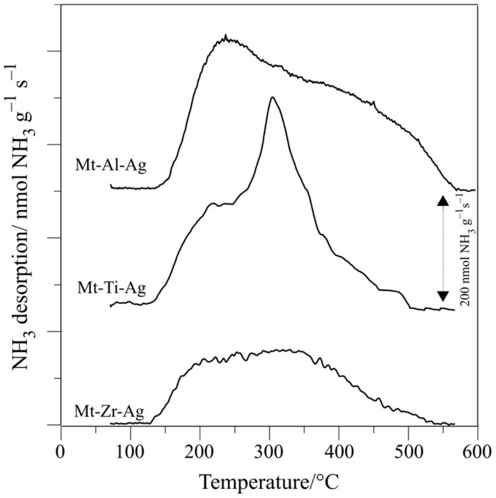

Fig. 4 NH$_3$-TPD profiles of alumina, titania and zirconia pillared clays modified with silver

that are represented by the sharp ammonia desorption peak at about 320°C. Additionally, modification of the TiO$_2$-pillared clay with Ag$^+$ cations decreased amount of strongly chemisorbed ammonia molecules that desorb above 400°C [10]. The ammonia desorption pattern recorded for the Mt-Zr-Ag catalyst is spread in the range of 130–540°C. Modification of the zirconia pillared clay with silver limited the amount of weak acidic centers, that corresponds to desorption of ammonia in the low temperature region of 150–300°C [11].

Results of NO-TPD measurements are presented in Fig. 5. The NO desorption pattern recorded for the Mt-Al-Ag catalyst consists of two maxima centered at about 150 and 370°C (Fig. 5a). It is supposed that nitric oxide chemisorbs on the two types of sites present on the surface of Mt-Al-Ag. Similar NO-TPD patterns were obtained for the alumina pillared montmorillonite that was not modified with transition metals [10]. So, it seems that NO chemisorption sites are localized mainly on the clay layers or alumina clusters. Analogous results were obtained for the Mt-Zr-Ag catalyst (Fig. 5c). In this case, the intensity of NO desorption was however significantly higher and formation of N$_2$O in the range of 325–370°C was detected. Evolution of oxygen was not observed. Probably, oxygen that was formed during conversion of NO into N$_2$O oxidized metallic silver to silver oxide. Desorption of nitric oxide from the Mt-Ti-Ag sample takes place in the range of 120–360°C with the maximum centered at about 240°C. Chemisorbed NO was partially decomposed to nitrogen and oxygen in the temperature range of 150–370°C. However, the evolution of N$_2$ in this temperature region was only detected. It is most likely that oxygen directly oxidizes silver to silver oxide. The NO desorption pattern does not contain peaks typical for TiO$_2$-pillared montmorillonites [8]. Thus, the majority of the surface in the Mt-Ti-Ag sample is covered with silver.

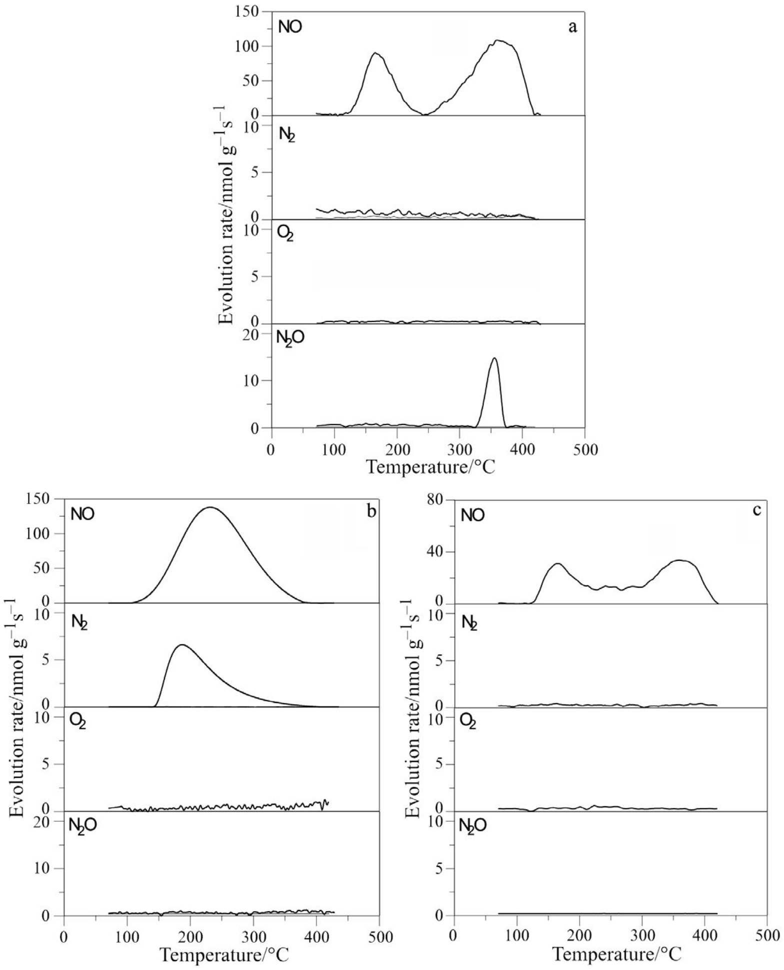

Fig. 5 NO-TPD profiles of alumina – a, titania – b, and zirconia – c pillared clays modified with silver

Conclusions

Large amount of silver introduced into the pillared clays by the ion-exchange method suggests that Ag exists on the montmorillonite surface of the form of metal oxide clusters rather than separate cations. Such silver oxide clusters are reduced to metallic silver during calcination of the samples at 400°C in the static air atmosphere.

The titania pillared clay modified with silver (Mt-Ti-Ag) was the most active catalyst for NO reduction by ethylene. Silver introduced into the zirconia or alumina intercalated montmorillonites activates them considerably less effectively. Significantly higher amounts of NO were converted by ammonia. The Mt-Ti-Ag clay was found to be the most active catalyst also for this process. In the presence of this catalyst, the NO conversion exceeded 90% in the temperature range of 270–400°C. At higher temperatures, the rate of NO reduction decreased due to the oxidation of ammonia by oxygen. Such an effect was not observed for the Mt-Al-Ag and Mt-Zr-Ag samples. However, the activity of these catalysts was lower than that of the Mt-Ti-Ag one. For all the clay catalysts the selectivity to nitrogen did not drop below 95% in the studied temperature range.

The TPD studies have shown that NO as well as NH_3 chemisorption sites exist on the surface of the modified clays. The ammonia desorption spectra obtained for the Mt-Al-Ag and Mt-Zr-Ag samples are very similar to those recorded for the alumina and zirconia pillared clays, respectively. Thus, the chemisorption of NH_3 molecules takes place mainly on the montmorillonites layers or pillars surface. In the case of the Mt-Ti-Ag sample, apart from maxima characteristic for the titania pillared clay, a new ammonia desorption peak, caused by the presence of silver, appeared.

At least two types of NO chemisorption sites on the surface of the Mt-Al-Ag and Mt-Zr-Ag samples were detected. The NO-TPD spectra recorded for these catalysts are very similar to those obtained for the alumina or zirconia intercalated clays. Thus, the NO chemisorption takes place mainly on the pillared montmorillonites surface. Totally different results were obtained for the Mt-Ti-Ag sample. In this case, a disappearance of maxima characteristic for the TiO_2 pillared clay and formation of new one, caused by the silver presence, was observed.

The new type of NO and NH_3 chemisorption sites that are present on surface of the Mt-Ti-Ag sample might be responsible for a high activity of this catalyst in the NO reduction processes.

* * *

This work was supported by KBN (Committee for Scientific Research, Poland) under contract No. 4T09B 06522.

References

1 M. Kubranova, E. Jona, E. Rudinska, K. Nemcekova, D. Ondrusova and M. Pajtasova, J. Therm. Anal. Cal., 74 (2003) 251.
2 Z. Yermiyahu, A. Landau, A. Zaban, I. Lapides and S. Yariv, J. Therm. Anal. Cal., 72 (2003) 431.
3 E. Kikuchi, T. Matsuda, H. Fujiki and Y. Merita, Appl. Catal., 11 (1984) 331.
4 J. R. Butruille and T. Pinnavaia, Catal. Today, 14 (1992) 141.
5 V. N. Parulekar and J. W. Hoghtower, Appl. Catal., 35 (1987) 263.
6 H. Mori, T. Okuhara and M. Misondo, Chem. Lett., (1987) 2305.
7 E. M. Serwicka, Polish J. Chem., 75 (2001) 307.
8 L. Chmielarz, R. Dziembaj, T. Łojewski, A. Węgrzyn, T. Grzybek, J. Klinik and D. Olszewska, Solid State Ionics, 141–142 (2001) 715.
9 L. Chmielarz, P. Kuśtrowski, M. Zbroja, A. Rafalska-Łasocha, B. Dudek and R. Dziembaj, Appl. Catal., B 45 (2003) 103.
10 L. Chmielarz, P. Kuśtrowski, M. Zbroja and R. Dziembaj, submitted to Appl. Catal. B.
11 L. Chmielarz, R. Dziembaj, T. Grzybek, J. Klinik, T. Łojewski and D. Olszewska, Catal. Lett., 70 (2000) 51.