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Modified layered clays as catalysts for ethanol oxidation

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ABSTRACT

Layered clays modified or not modified and promoted with copper cations were studied in catalytic oxidation of ethanol, representing volatile organic compounds (VOC). The influence of preparative steps, such as acidic activation and pillaring was considered. The catalysts were characterized by the low-temperature sorption of N_2, temperature-programmed reduction (TPR), transmission electron microscopy (TEM) and tested in the reaction of the ethanol oxidation.

The promotion with CuO is the most important step in the preparation of catalysts and proved to increase their activity and selectivity. The pillared clays promoted with CuO are promising catalysts for ethanol oxidation.

1. Introduction

Volatile organic compounds in industrial outgases present a serious environmental problem. VOCs are pollutants produced by different types of industry [1,2]. One of the possible methods of the reduction of VOC emissions is the catalytic oxidation using different catalysts containing noble or transition metals [3–16].

Noble metals such as supported Pt or Pd were found to be very active at lower temperatures [17–24]. Santos et al. studied oxidation of ethanol on Pt, Pd, Ir, Rh or Au supported on TiO_2 introduced by incipient wetness technique and liquid phase reduction deposition [24]. T_{100} was between 283 and 380 °C, depending, firstly, on the metal choice and secondly, on the method of active material introduction. When impregnation was used T_{100} were ca. 20 °C higher than for the introduction of active material by liquid phase reduction deposition. It should be taken into account, however, that noble metals are expensive and not abundant and this is why metal oxide catalysts have been considered as a low cost alternative. Oxides, single or mixed, without a support and with support, were studied for different VOC oxidation. Cu, Ag, Mn and Fe were recognized as promising active materials [11]. CuO_x unsupported and supported, single or mixed with other oxides were studied for oxidation of different volatile organic coumpounds (VOC). Morales et al. [25] studied unsupported Mn–Cu oxides for total oxidation of ethanol. CuO showed 100% conversion at ca. 260 °C. Delimaris and Ioannides [26] studied oxidation of C_2H_5OH over CuO–CeO_2 catalysts. On CuO reaction started at ca. 170 °C and reached 100% around 320 °C but below 275 °C selectivity to CO_2 was low and considerable amounts of acetaldehyde were obtained [26]. Cordi et al. studied C_2H_5OH oxidation on Cu/Al_2O_3. Between ca. 250 and 300 °C very small amounts of C_2H_4O were registered. CO_2 was accompanied by small amounts of CO at 200–370 °C [27]. Thus temperatures under 300 °C do not seen practical for C_2H_5OH removal by total oxidation. Cu supported on zeolites was also considered. Chen et al. studied oxidation of acetone, ethyl acetate and toluene over Cu supported on cerium-modified and zirconium pillared clays. T_{98} for toluene was ca. 300 °C but the publication lacks detailed experimental conditions (flow rate, stability, etc.) [28]. Wang et al. studied toluene oxidation on Cu/Al_2O_3 and other supported. T_{90} for 5% $MeO_x/\gamma Al_2O_3$ was: 315, 327, 347, 387, 390 °C, for Me = Cu, Fe, Cr, Mn, Co, respectively [29]. Oxidation of toluene on CuO–MnO_x on different supports was compared by Li et al. [30,31]. Activity formed a sequence: Cu–Mn/ZSM-5-25 > Cu–Mn/ZSM-5-38 [32]. For MCM-supports the activity sequence was: Cu–Mn–MCM-41 > Cu–MCM-41 > Mn–MCM-41. Maximum conversion was obtained at ca. 350–450 °C.

TPO studies of ethanol oxidation on Ag/Al_2O_3 showed maximum CO_2 formation at ca. 350 and 500 °C, while maximum CO formation was registered at 400 and 600 °C. Very small amounts of ethene were formed with a maximum at ca. 325 °C, with the formation of C_2H_4O at lower temperatures [32]. Many authors reported that perovskites of $LaMeO_3$ formula (Me = Mn, Co, Ni) are also suited for total oxidation [14,33–35]. Doping with Ag atoms improved activites of metal oxides due to greater oxygen storage [36].

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Table 1
The applied preparation steps for the catalysts and specific surface area.

Samples	VER-Cu1	VER-Cu3	VER-Ag1	VER-Ag3	BAlCu	BHCu	BHAlCu
Acidic activation	–	–	–	–	–	+	+
Intercalation	–	–	–	–	+	–	+
3% $Cu(NO_3)_2$ or 3% $AgNO_3$ adsorption	–	+	–	+	–	–	–
Cu or Ag 1% impregnation	+	–	+	–	–	–	–
Cu 5% impregnation	–	–	–	–	+	+	+
S_{BET} (m^2/g)	1	2	nm	nm	50	142	145

Copper and silver based catalysts are often studied. There are, however, rather few papers describing the application of layered clays for VOC removal [8–10,12,28,37–39]. Clays are quite attractive because they are cheap natural materials and there are several modification possibilities. Both textural and chemical properties e.g. basic/acidity may be changed through appropriate preparation procedures. Typical preparation steps used to tailor chemical and physical structures of layered clays are acidic/basic treatments, intercalation of hydroxycations, called pillaring, and promoting with transition metal oxides/hydroxides. [25,26,28,29,38,40–42].

The subject of the work, a first in a series, was to study the influence of different preparation parameters of clays (treated as supports for copper species) on the ethanol oxidation properties. The influence of a second oxide to Cu- or Ag-promoted catalysts will be the next step in the study.

2. Experimental

2.1. Catalysts

The starting clays were commercial vermiculite (Sigma–Aldrich GmBH) (designation VER), and bentonite (Riedel-de Haën) (designation B). Vermiculite was used as obtained, while bentonite was prepared according to three routes, consisting of a different number of treatment steps. Route 1: bentonite (further designation: B) → pillaring BAl; Route 2: bentonite B → acidic pretreatment → BH; Route 3: bentonite B → acidic pretreatment → pillaring → BHAl.

Pillaring was carried out with Al–polycations (designation “Al”) with chlorhydrol according to the procedure described by Vaughan and Lussier [43]. An acidic pretreatment of clays was carried out with 20% HCl solution at a boiling temperature for 1 h, an activation time was chosen basing on previous experiments [44].Cu oxides were introduced either by adsorption (vermiculite, bentonite treated with acid) or by the incipient wetness method (pillared bentonite). For the former, a determined amount of mineral was introduced into the $Cu(NO_3)_2$ solution and mixed for 2 h, filtered and dried at room temperature. For the latter, the incipient wetness method was chosen, because pretreatment of layered clays may decrease their exchange capacity. Before catalytic tests all samples were calcined in situ at 500 °C for 30 min. Since, during the catalytic tests, vermiculites exchanged with Cu proved to be most active and selective of the studied samples, additionally, for comparison, this type of clay was promoted with Ag, using $AgNO_3$ and applying the same procedure as for VER-Cu. The list of the studied catalysts, together with the applied preparation steps, is summarized in Table 1.

2.2. Characterization

The characterization of the samples included: (i) S_{BET} determined by nitrogen sorption at 77 K using a volumetric method (Micromeritics ASAP 2010). Prior to sorption the samples were outgassed at 200 °C for 16 h. (ii) TPR-H_2 by Autochem 2910. (iii) Distribution of an active material by Transmission Electron Microscopy (TEM) was registered using the TEM – 1011 with Teola film, acceleration voltage 100 kV and tungsten (W) gun.

Catalytic properties in ethanol oxidation (EtOH conversion to CO_2 and CO) were studied under the following conditions: mass of catalyst 200 mg, flow rate 250 cm^3/min; reaction mixture: 1000 ppm EtOH, 7% O_2, rest He; reaction temperatures 250, 300, 350 and 400 °C. After calcination the temperature was decreased under helium to 250 °C and the gas flow was switched to the reaction mixture. After 60 min online, temperature was raised by 50 °C and the next experimental point was measured. The reaction products were analyzed in the Siemens analyzer containing the CO_2 and CO detector – Ultramat 6E. Activity of catalysts was defined as % of C_2H_5OH turned into % of CO_2 and CO. Selectivity towards CO_2 was defined as: $S_{CO_2} = \%_{CO_2}/\%_{CO_2} + \%_{CO}$.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Specific surface area

Table 1 summarizes specific surface areas for the studied catalysts. Vermiculite is characterized by low S_{BET} which additionally decreased after the Cu promotion. Bentonite pillared with Al showed moderate S_{BET} (123 m^2/g), which decreased after the promotion with Cu (to 50 m^2/g). Samples treated with acid, either pillared or not pillared, subsequently promoted with Cu (BHCu, BHAlCu) showed higher S_{BET} than BAlCu. This could have been caused by a different distribution of active material.

3.1.2. Reducibility

Fig. 1a summarizes the TPR profiles for the studied samples. Vermiculites exchanged with Cu showed the identical reducibility, independently of the concentration of the applied exchange solution, in contrast to vermiculites exchanged with Ag.

All CuO promoted catalysts have two peaks corresponding to different types of redox sites. According to Dow et al. [45], the first (low-temperature) maximum may be ascribed to a highly dispersed copper oxide, while the second to bulky CuO. An acidic activation of bentonite (BHCu) shifted the reduction peaks to lower temperatures – two distinct maxima are present at 230 °C and 270 °C, and an indistinct shoulder at ca. 350 °C. Bentonite pillared by alumina and promoted with Cu (BAlCu) has a large peak at ca. 380 °C, with an indistinct shoulder at lower temperatures, around 300 °C. The application of both procedures, acidic treatment and pillaring, led to a decrease in temperature of TPR maximum and the peak was registered at ca. 290 °C and a small shoulder at 400 °C (BHAlCu).

For VER-Ag3 the TPR-H_2 peaks were found with maxima at ca. 420 °C and 610°C. In case of pure vermiculite no peaks were observed. Thus clays promoted with CuO have at least two different types of Cu-species, both the type and number dependent on the preparation procedure. This is in agreement with the obser-

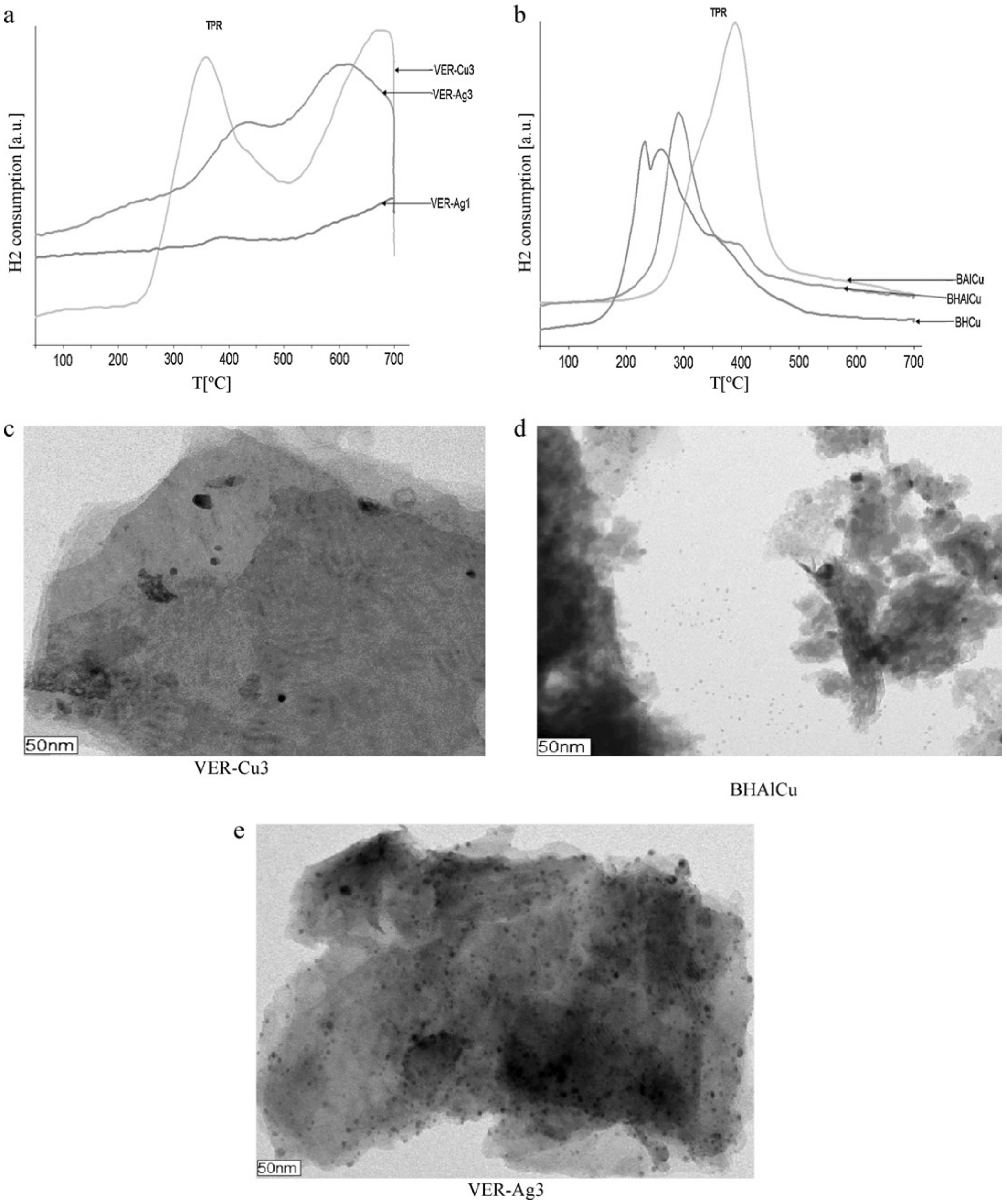

Fig. 1. (a and b) TPR-H_2 profiles for the studied catalysts. (c–e) TEM studied catalysts.

vations of Knapczyk et al. [46], who found types and number of CuO species introduced onto layered clays being dependent on the preparation steps, among others on the type of pillars.

The number of sites depends strongly on the treatment of the support for B clays.

3.1.3. TEM

Materials containing silver show a much higher distribution (cp. Fig. 1c–e) than respective supports promoted with Cu. Silver is well distributed over the surface of the tested samples. Copper generally is not uniformly distributed. In the case of Cu, numerous bigger aggregates may be observed. In some samples, e.g. VER-Cu3 active material was observed on the outer surface of the carrier particles. During the TEM studies no pillaring material (aluminum) could be distinguished.

3.1.4. Catalytic activity

Fig. 2a and b compare activity and selectivity towards CO_2 for all studied catalysts. The onset of reaction was around 250 °C for all studied samples, except for VER-Ag1 (onset at 300 °C). For promoted vermiculites conversion to CO_x ($CO_2 + CO$) at temperatures of 300 °C, 350 °C and 400 °C formed a sequence: VER-Cu3 > VER-Ag3 > VER-Cu1 > VER-Ag1. Selectivity towards CO_2 for VER-Ag3 and VER-Cu3 was over 99%, for VER-Cu1 and VER-Ag1 was over 97%, respectively.

The activity in total oxidation of ethanol by differently modified bentonite promoted with Cu at temperatures of 250 °C and 300 °C, formed a sequence: BAlCu ≈ BHAlCu > BHCu while at 350 °C and 400 °C a sequence: BAlCu > BHAlCu > BHCu. Selectivity towards CO_2 was lower than for vermiculites and formed a sequence: BAlCu > BHCu > BHAlCu in a temperature range 250–400 °C. The studied catalysts behaved differently with time, as illustrated for VER-Cu3 and BHAlCu in Fig. 2c and d. Conversion to CO_x VER-Ag3,

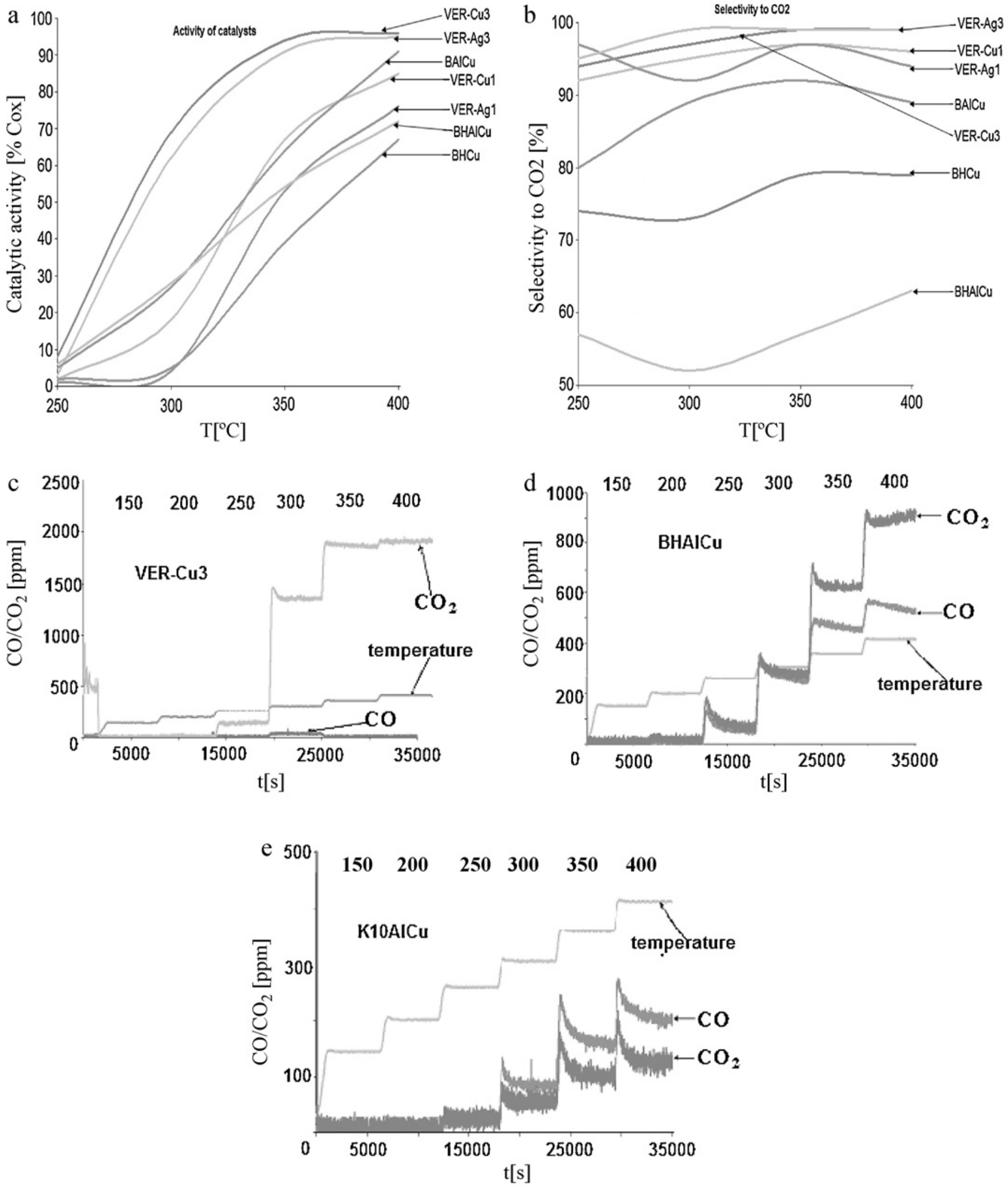

Fig. 2. (a) Conversion to CO_x ($CO_2 + CO$); (b) selectivity to CO_2; (c–e) the amount of CO_2 and CO in the products as a function of TOS.

and VER-Ag1, VER-Cu1, VER-Cu3 was also stable within 60 min TOS, while BHCu deactivated similarly as BHAlCu. In order to check if an increased acidity influenced stability, a commercial acidic montmorillonite K10 was promoted with Cu (designation K10Cu) or pillared with Al hydroxycations and promoted with Cu. In both cases, deactivation with TOS was observed (cp. Fig. 2e for K10AlCu). The activity of the samples based on clays with an increased acidic character obtained by an acidic treatment (BHCu and BHAlCu) decreased with time. This is in agreement with the general tendency of catalysts containing acidic surface species for coking.

From textural and reducibility measurements the following may be concluded:

- There is no correlation of activity or selectivity with specific surface area S_{BET}. Promoted vermiculites had the lowest S_{BET} and the highest activity and selectivity.
- Reducibility plays an important role for all catalysts, but both the temperature of TPR maximum and the number of reducible CuO-species are of importance.

As described above, all B-derived catalysts have both low and medium-temperature TPR peaks; the former cannot be correlated with activity presented in Fig. 2a. However, since both BHAlCu and BHCu suffered a severe deactivation, it is reasonable that sites with the easiest reducibility are first eliminated by coking. On the other hand, the number of medium-temperature redox sites correlates well with activity (cp. Fig. 2a). Similarly, vermiculites promoted with CuO, which showed higher activity and did not show deactivation during 60 min TOS did not contain the sites with the lowest reducibility. Taking into account the studies of Dow et al. [45] concerning the interpretation of low and medium TPR-H_2 peaks, as belonging either to highly dispersed or to bulky CuO oxides, it must be concluded that the latter are more advantageous for total oxidation. This is in agreement with the findings of Santos et al. [24] who studied VOC (ethanol, toluene) oxidation by noble metals supported on TiO_2 and found that activity doubled as the average particle of Pt or Pd increased, respectively, from 3.6 to 5.4 nm and

4.0 to 7.2 nm [24]. Other preparation steps, typically used for tailoring textural, structural and chemical properties of clays do not lead to the improvement of catalytic properties in the studied reaction. Especially, the acidic treatment, which was proven to increase the activity and selectivity of such materials in other reactions, e.g. in the selective catalytic reduction of NO with ammonia [47,48], led to the deterioration of activity, selectivity towards CO_2 and stability in ethanol oxidation.

4. Conclusions

CuO-promoted natural clays may be considered promising catalysts for total oxidation of VOCs. Their activity is lower than in case of noble metals, but they are much cheaper and their preparation is easier. Promotion with CuO is the most important step in the preparation and vermiculites-CuO proved to be the best of the studied clay catalysts with the highest activity and good selectivity, despite their low specific surface area. Other preparation steps, such as the acidic treatment or pillaring did not lead to the improvement of the activity, selectivity towards CO_2 or stability.

TPR measurements showed at least two different types of CuO sites, interpreted as highly dispersed and bulky CuO. The latter seems to play a major role in total VOC oxidation.

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References

[1] M.J. Molina, Pure Appl. Chem. 68 (1996) 1749.
[2] R. Atkinson, Atmos. Environ. 34 (2000) 2063.
[3] M. Lamallem, H. El Ayadi, C. Gennequin, R. Cousin, S. Siffert, F. Aïssi, A. Aboukaïs, Catal. Today 137 (2008) 367.
[4] M.A. Centeno, M. Paulis, M. Montes, J.A. Odriozola, Appl. Catal. A 234 (2002) 65.
[5] R. Dula, R. Janik, T. Machej, J. Stoch, R. Grabowski, E.M. Serwicka, Catal. Today 119 (2007) 327.
[6] J. Łojewska, A. Kołodziej, T. Łojewski, R. Kapica, J. Tyczkowski, Catal. Commun. 10 (2008) 142.
[7] J. Łojewska, A. Kołodziej, R. Kapica, A. Knapik, J. Tyczkowski, Catal. Today 1475 (2009) 594.
[8] N.R. Sanabria, M.A. Centeno, R. Molina, S. Moreno, Appl. Catal. A 356 (2009) 243.
[9] L.M. Martínez T, M.I. Dominguez, N. Sanabria, W.Y. Hernandez, S. Moreno, R. Molina, J.A. Odriozola, M.A. Centeno, Appl. Catal. A 364 (2009) 166.
[10] J.G. Carriazo, L.M. Martínez, J.A. Odriozola, S. Moreno, R. Molina, M.A. Centeno, Appl. Catal. B 72 (2007) 157.
[11] W.B. Li, J.X. Wang, H. Gong, Catal. Today 148 (2009) 81.
[12] T. Mishra, P. Mohapatra, K.M. Parida, Appl. Catal. B 78 (2008) 279.
[13] M. Raciuleta, P. Afanasiev, Appl. Catal. A 388 (2009) 79.
[14] A. Musialik-Piotrowska, H. Landmesser, Catal. Today 137 (2008) 357.
[15] J. Łojewska, A. Kołodziej, J. Żak, Polish J. Chem. Technol. 9 (1) (2007) 15–19.
[16] Y. Li, X. Zhang, H. He, Y. Yu, T. Yuan, Z. Tian, J. Wang, Y. Li, Appl. Catal. B 89 (2009) 659.
[17] J. Carpentier, J.F. Lemonier, S. Siffert, H. Laversin, A. Aboukais, Appl. Catal. A 234 (2002) 91.
[18] M. Paulis, L.M. Gandia, A. Gil, J. Sambeth, J.A. Odriozola, M. Montes, Appl. Catal. B 26 (2000) 37.
[19] K. Okumara, T. Kobayashi, H. Tanaka, M. Niwa, Appl. Catal. B 44 (2003) 325.
[20] K. Okumara, H. Tanaka, M. Niwa, Catal. Lett. 58 (1999) 43.
[21] T. Takeguchi, S. Aoyama, J. Ueda, R. Kikuchi, K. Eguchi, Top. Catal. 23 (1–4) (2003) 159.
[22] S. Ordonez, L. Bello, H. Sastre, R. Rosal, F.V. Diez, Appl. Catal. B 38 (2002) 139.
[23] M. Paulis, M. Peyrard, M. Montes, J. Catal. 199 (2001) 30.
[24] V.P. Santos, S.A.C. Carabineiro, P.B. Tavares, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, Appl. Catal. B 99 (2010) 198.
[25] M.R. Morales, B.P. Barbero, L.E. Cadús, Fuel 87 (2008) 1177.
[26] D. Delimaris, T. Ioannides, Appl. Catal. B 89 (2009) 295.
[27] E.M. Cordi, P.J. Neill, J.L. Falkoner, Appl. Catal. B 14 (1997) 23.
[28] M. Chen, L. Fan, L. Qi, X. Luo, R. Zhou, X. Zheng, Catal. Commun. 10 (2009) 838.
[29] Ch.-H. Wang, S.-S. Lin, Ch.-L. Chen, H.-S. Wenig, Chemosphere 64 (2006) 503.
[30] W.B. Li, M. Zhuang, T.C. Xiao, M.L.H. Green, J. Phys. Chem. B 110 (2006) 21568.
[31] W.B. Li, M. Zhuang, J.X. Wang, Catal. Today 137 (2008) 340.
[32] E.M. Cordi, J.F. Falconer, Appl. Catal. A 151 (1997) 179.
[33] S. Irusta, M.P. Pina, M. Menendez, J. Santamaria, J. Catal. 179 (1998) 400.
[34] G. Sinquin, C. Petit, S. Libs, J.P. Hindermann, A. Kinnemann, Appl. Catal. B 32 (2001) 37.
[35] V. Blasin–Aube, J. Belkouch, L Monceaux, Appl. Catal. B 43 (2003) 175.
[36] N. Watanabe, H. Yamashita, H. Miyadera, S. Tominaga, Appl. Catal. B 8 (1996) 405.
[37] R. Beauchet, P. Magnoux, J. Mijoin, Catal. Today 124 (2007) 118.
[38] C.T. Wong, A.Z. Abdullah, S. Bhatia, J. Hazard. Mater. 157 (2008) 480.
[39] L.C.A. Oliveira, R.M. Lago, J.D. Fabris, K. Sapag, Appl. Clay Sci. 39 (2008) 218.
[40] M. Motak, Catal. Today 137 (2008) 247.
[41] Ch.-H. Wang, Chemosphere 55 (2004) 11.
[42] H.L. Tidahy, S. Siffert, F. Wyrwalski, J.-F. Lamonier, A. Aboukaïs, Catal. Today 119 (2007) 217.
[43] D.E.W. Vaughan, R.J. Lussier, in: L.W. Rees (Ed.), Proc. 5th Int. Conf. Zeolites, vol. 94, Heyden, London, 1980.
[44] T. Grzybek, M. Motak, H. Papp, Catal. Today 90 (2004) 69.
[45] W.-P. Dow, Y.-P. Wang, T.-J. Huang, J. Catal. 160 (1996) 155.
[46] M. Knapczyk, M. Motak, W. Suprun, H. Papp, T. Grzybek Catal. Today, (2011) doi:10.1016/j.cattod.2010.11.073.
[47] T. Grzybek, D. Olszewska, H. Papp, Pol. J. Environ. Stud. 11 (Suppl. 3) (2002) 11.
[48] B. Samojeden, J. Klinik, T. Grzybek, H. Papp, Gospodarka Surowcami Mineralnymi 24 (2008) 295.