Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 137 (2008) 340–344
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Catalytic combustion of toluene on Cu-Mn/MCM-41 catalysts: Influence of calcination temperature and operating conditions on the catalytic activity

W.B. Li [a,b,*], M. Zhuang [b], J.X. Wang [a]

[a] *Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China*
[b] *Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, PR China*

Abstract

Catalytic combustion of toluene on Cu-Mn/MCM-41 catalyst was performed in tubular flow reactor operated at atmospheric pressure. The effect of catalyst pre-treatment temperatures on the catalytic activity and stability was investigated. Some reaction variables, such as inlet concentration of toluene and oxygen, reaction temperatures and space velocities were varied over wide ranges, and the influence of different reaction conditions on toluene conversion was discussed. It is showed that the catalytic activity was significantly affected by calcination temperatures between 300 and 800 °C, and oxygen concentration, toluene concentration and space velocity are all key experimental factors to optimize the toluene combustion activities. The objective of this study was to investigate catalytic properties of Cu-Mn/MCM-41 catalysts prepared at different calcination temperatures, in order to obtain additional information to prepare an efficient and highly active catalyst at low temperature.

Keywords: Toluene; Catalytic combustion; MCM-41; Cu Oxide/Mn oxide

1. Introduction

Catalytic combustion at a lower temperature is an effective route to eliminate volatile organic compounds (VOCs) [1]. Various kinds of catalysts were investigated for the catalytic combustion of VOCs, for example, supported noble metals such as Pd/Mg–Al hydrotalcite [2], Pd/Al_2O_3 [3], Pd/ZrO_2 [4,5], PdO/SnO_2 [6], platinum-containing monolithic carbon aerogels [7], Pt/Al_2O_3 [8,9], supported metal oxides such as Cu–CuNaHY [10], Cu/Mg/Al hydrotalcites [11] [2–3], Cu/TiO_2 [12], Zn–Co/Al_2O_3 [13], gold/cerium oxide [14], gold/iron oxide [15], silica supported U_3O_8 [16], V/$MgAl_2O_4$[17], mixed metal oxides such as Co–Fe–Cu mixed oxides [18], Mn-doped ZrO_2[19], Fe-doped ZrO_2[20,21].

Okumura et al. [4] have recently reported that the oxide support might play a significant role for the Pd supported catalysts on the catalytic combustion of toluene. Antunes et al. [10] have reported that CuNaHY zeolites show high toluene combustion activity and serious deactivation at low temperatures due to the formation of carbonaceous deposits (coke) retained inside the zeolite pores during the reaction. On the other hand, MCM-41 possesses high BET surface area, uniform pore sizes with larger pore dimensions between 1.5 and 10 nm, and high thermal and hydrothermal stability [22]. Moreover, MnO_x–ZrO_2 and CuO_x–MnO_x mixed oxides prepared in reverse microemulsion show higher specific surface areas and superior high toluene combustion activity [19].

Our more recent study [23] have indicated that that mesoporous catalysts have exhibited the highest catalytic activity as compared to microporous catalysts for catalytic combustion of toluene in the presence of excess oxygen, where the reaction activity followed the order of Cu-Mn/MCM-41 > Cu-Mn/ZSM-5 > Cu-Mn/β-zeolite > Cu-Mn/porous silica, and meanwhile coke formation could be effectively minimized for the combustion of toluene. Following the above study, we report here the further results on the effect of the various experi-

---

* Corresponding author at: Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China.
E-mail addresses: wblichem@yahoo.com.cn, wbli@tsinghua.edu.cn (W.B. Li).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.11.002

mental parameters on the catalytic activities of the novel Cu-Mn/MCM-41 catalysts for the combustion of toluene.

2. Experimental

2.1. Synthesis of Cu-Mn/MCM-41

The siliceous MCM-41 was prepared in a similar procedure as reported elsewhere [23,24] using the following gel composition: (1.0 SiO_2):(0.4 CTAB):(1.6 TMB):(12.2 NH_4OH):(53 Ethanol):(171 H_2O), where CTAB and TMB denote cetyltrimethylammonium bromide and trimethylbenzene, respectively. Tetraethoxysilane was used as silica precursor. These mixtures were transferred into a Teflon beaker and sealed for 24 h at 25 °C. The obtained solid material was filtered, washed, dried at 25 °C and calcined with heating rate of 10 °C/min in flowing nitrogen up to 550 °C and then in air at 550 °C for 3 h. These samples are referred to as MCM-41. The thus obtained MCM-41 powders were ion exchanged with citric acid and then ion exchanged with known concentrations of aqueous solutions of $Cu(CH_3COO)_2$ and $Mn(CH_3COO)_2$. The final samples were denoted as Cu-Mn/MCM-41 after being filtered, washed, dried in air at 120 °C for 24 h and then calcined at 450 °C. These final samples were calcined at 300–800 °C followed by being crushed and sieved as 0.10–0.150 mm and then ready for the catalyst tests.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns were obtained on Rigaku D/max RB X-ray diffractometer using Cu Kα radiation. Nitrogen adsorption and desorption isotherms were determined at −196 °C by means of Micromeritics ASAP 2010 surface area analyzer, from which BET surface areas were calculated and the pore volumes were determined using the procedure proposed by Barrett, Joyner and Halenda (BJH). Elemental analysis was performed with X-ray fluorescence (XRF) analyzer on Shimadzu XRF-1700 spectroscopy. Transmission electron microscope (TEM) images were obtained on a JEM-200C transmission microscope. Scanning electron microscope (SEM) images were taken on the JSM-6301F instrument with pre-coating samples with gold.

2.3. Catalytic activity measurements

Catalytic activities were measured in a 10 mm i.d. quartz tubular reactor. The reaction mixture consisting of toluene (0.35–2% by volume), O_2 (1.5–18.3% by volume) and argon (balance gas) was passed continuously through a 0.1 g catalyst sample layer with a total flow rate of 60–350 ml/min of argon. The inlet and outlet gas compositions were analyzed after stepwise changes in the reaction temperatures by on-line gas chromatograph (Shimatzu 14B) with a FID detector using a Porapak Q column.

3. Results and discussion

3.1. Characterization of Cu-Mn/MCM-41 catalysts

A Cu-Mn-MCM-41 sample was obtained and analyzed by nitrogen adsorption/desorption, and its BET surface area was 1043 m^2/g after calcinations at 550 °C by BJH method with average pore size at 2.97 nm.

TEM images of the calcined Cu-Mn-MCM-41 materials showing the highly ordered hexagonal pore arrangement as shown in Fig. 1, which is in good agreement with the XRD data in the previous report [23], where the sharp and intense XRD peaks of Cu-Mn/MCM-41 calcined at 550 °C remained to be typical of mesoporous, indicating that these materials have much stable and highly ordered mesoporous pore structures.

SEM was used to illustrate morphological structures of Cu-Mn/MCM-41 calcined at 550 °C. Fig. 2 shows the rice-particle-like morphological structures with a diameter around 0.5 μm, and most of the particles appeared as uniform particle sizes.

3.2. Effect of calcination temperatures

Generally calcination of the catalysts might lead to sintering of active species on the catalyst. The effect of calcination temperature on conversion of toluene during its catalytic combustion at different reaction temperatures was investigated.

The comparison of toluene conversions obtained for the catalyst calcined at temperature of 300–800 °C is shown in Fig. 3. The results indicate that operating window (the range of temperature where the catalyst has high activity) is shifted to the range of higher reaction temperatures and broadened with the increase in calcination temperature. Comparing the catalyst activity at one typical temperature (e.g., 300 °C), it can be seen that the toluene conversion decreases from 87.1 to 0% with an increase of calcination temperature from 300 to 800 °C. However, even catalyst pre-treated at 800 °C shows very high and stable activity at reaction temperature higher than 300 °C. Therefore, thermal treatment at higher temperatures probably

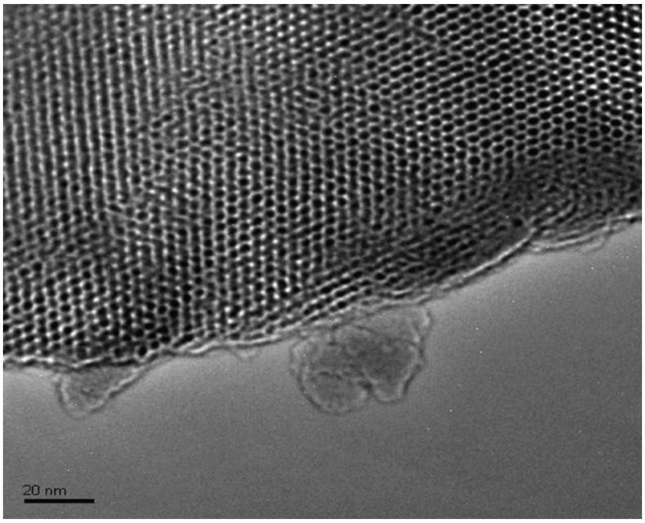

Fig. 1. TEM image of the Cu-Mn/MCM-41 catalyst calcined at 550 °C.

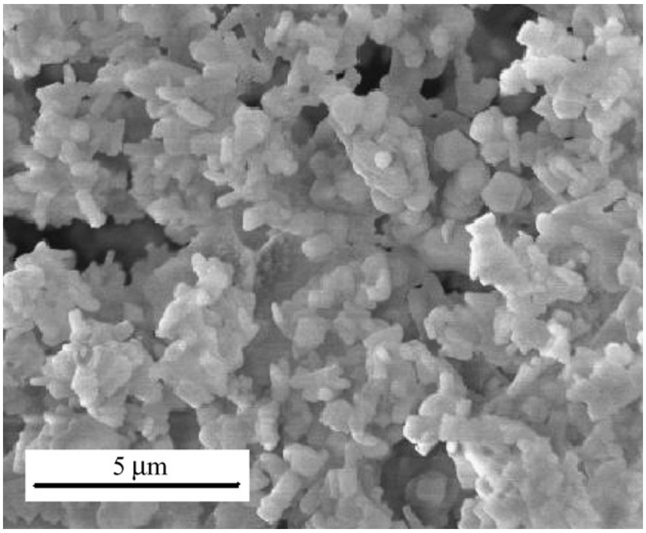

Fig. 2. SEM image of the Cu-Mn/MCM-41 catalyst calcined at 550 °C.

leads to partial sintering of the active species on the catalyst surface as reported on $Mn_{0.4}Zr_{0.6}$ mixed oxide catalyst for the combustion of toluene [19], and hence affects the redox properties responsible for high activity of the catalyst in the employed reaction system. The sintering of the Cu and Mn species was further evidenced by XRD analysis of the Cu–Mn/MCM-41 discussed later.

Fig. 4 shows the XRD analysis of Cu-Mn/MCM-41catalyst after calcinations at elevated temperatures. It is observed that below 550 °C, the catalyst was amorphous or nano-crystallite due to their crystal sizes below the value of detection limit of the X-ray technique. When heating the catalyst to 800 °C, the XRD patterns of the samples showed the characteristic peaks of CuO and $CuMn_2O_4$ supported on MCM-41, indicating the growth of the crystal sizes of the Cu and Mn species on the sample. The results also imply that the highly dispersed structures of CuO and $CuMn_2O_4$ supported on MCM-41 are responsible for the high activity of the combustion reaction.

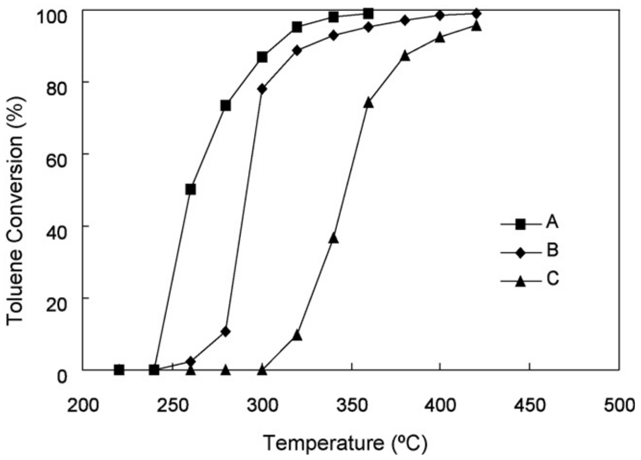

Fig. 3. Toluene conversion vs. reaction temperature over the Cu-Mn/MCM-41 sample calcined at various temperatures: (A) 300 °C; (B) 550 °C and (C) 800 °C. Reaction condition: catalyst weight = 0.1 g; total flow rate = 60 cm^3/min; toluene concentration = 3500 ppm.

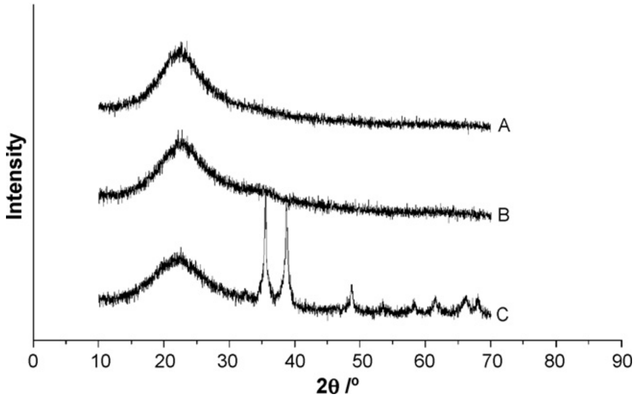

Fig. 4. XRD Pattern of the Cu-Mn/MCM-41 catalysts calcined at various temperatures: (A) 300 °C; (B) 550 °C and (C) 800 °C.

It is reasonable to propose that the sintering of the catalyst may play a major role in the catalyst deactivation during calcinations of the catalyst, but Fig. 3 also shows that the activity of toluene conversion remained high, i.e., 99.1 and 95.4% at 360 °C, on the Cu-Mn/MCM-41 catalyst after calcinations up to 550 and 800 °C, respectively, which is indicating that the Cu-Mn/MCM-41 catalyst is relatively thermally stable.

3.3. Effect of the inlet toluene concentration

Fig. 5 shows the conversion as a function of temperature over Cu-Mn/MCM-41catalyst under different toluene concentrations (3500, 10,500, 20,000 ppm). For a toluene concentration of 3500 and 10,500 ppm, the conversion was 95.2 and 88.6%, respectively, at a reaction temperature of 320 °C; and when increasing the concentration to 20,000 ppm, the conversion decreased to only 14.2% at a reaction temperature of 320 °C. These results indicate that increasing reactant concentration results in decreasing activity. Such a phenomenon is normal for catalytic oxidation of VOC, i.e., the lower the concentration, the lower the light-off temperature as reported for the toluene combustion on 5 wt.% Cu/γ-Al_2O_3

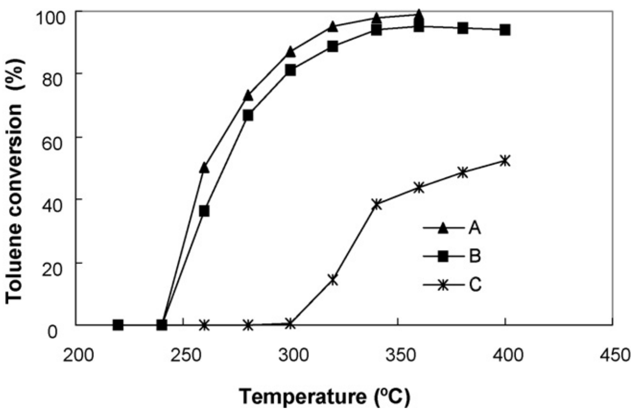

Fig. 5. Toluene conversion vs. reaction temperature over the Cu-Mn/MCM-41 sample under various toluene concentrations: (A) 3500 ppm; (B) 10,500 ppm and (C) 20,000 ppm. Reaction condition: catalyst weight = 0.1 g; total flow rate = 60 cm^3/min; oxygen concentration = 8.8%.

[25]. It is observed that an increase in the inlet toluene concentration from 3500 to 10,500 ppm has small influence on toluene conversion over the whole range of the reaction temperature. However, further increase of inlet toluene concentration to 20,000 ppm leads to a decrease in toluene conversion. At the same time, the range of operating window is shifted to the higher temperature (above 300 °C).

3.4. *Effect of the inlet oxygen concentration*

Since oxygen content is generally essential for the combustion reaction, therefore the effect of oxygen content on toluene conversion over the Cu-Mn/MCM-41 catalyst was shown in Fig. 6. Under 1.5% oxygen by volume, toluene conversion at a reaction temperature of 320 °C was only 12.5%, while the conversion increased to 77.8% with increasing oxygen content to 4.0% by volume, and reached 95.2 and 97.8% with further increasing the oxygen content to 8.8 and 18.3%, respectively. As expected, toluene conversion increases with the increase in the inlet oxygen concentration. The same trend is observed over the whole range of reaction temperatures, and is shown more obvious below 8.8% of oxygen concentration.

On the other hand, it is observed that the black and slightly sticky products were available on the reaction chamber at a lower oxygen concentration, where a partial polymerization of toluene occurred, which is similar with the report by Tidahy et al. [26] for the oxidation of toluene and chlorobenzene over Pd/TiO_2–ZrO_2 and Pd/TiO_2 at low temperature; therefore, it is essential to supply enough oxygen content to the feed gas in order to obtain the complete oxidation of toluene.

3.5. *Effect of the space velocity*

The performance of the Cu-Mn/MCM-41 catalyst in the toluene combustion was also studied at different space velocities. Fig. 7 shows the influence of space velocity on the toluene combustion as a function of reaction temperatures. From 18,000 to 36,000 h^{-1}, the toluene conversion remained almost unchanged, while further increasing the space velocity to 72,000 h^{-1} led a decrease in the combustion activity. Above 360 °C, the catalyst shows high toluene conversion, i.e., 86%, even at a very high space velocity of 72,000 h^{-1}. The similar results were also reported for combustion of dilute toluene and methyl ethyl ketone over transition metal-doped zirconia catalysts [21].

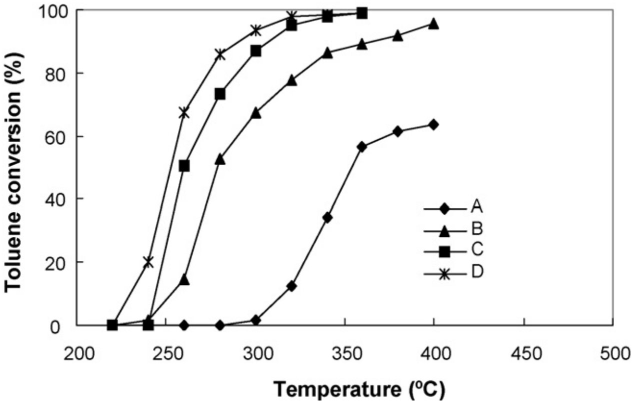

Fig. 6. Toluene conversion vs. reaction temperature over the Cu-Mn/MCM-41 sample under various oxygen concentrations: (A) 1.5%; (B) 4.0%; (C) 8.8% and (D) 18.3%. Reaction condition: catalyst weight = 0.1 g; total flow rate = 60 cm^3/min; toluene concentration = 3500 ppm.

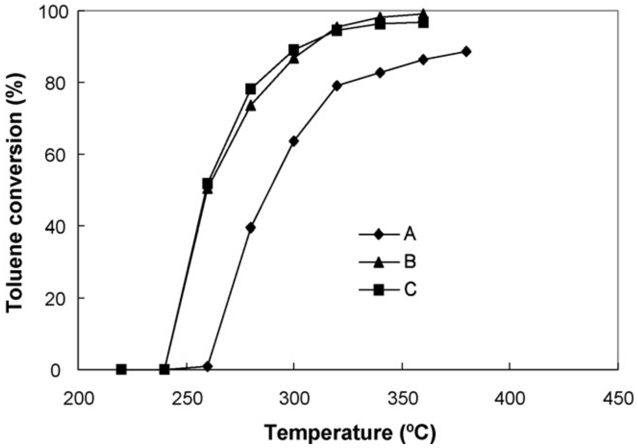

Fig. 7. Toluene conversion vs. reaction temperature over the Cu-Mn/MCM-41 sample under various space velocities: (A) 72,000 h^{-1}; (B) 36,000 h^{-1} and (C) 18,000 h^{-1}. Reaction condition: catalyst weight = 0.1 g; toluene concentration = 3500 ppm; oxygen concentration = 8.8%.

According to the literature reports, some perovskite catalysts and supported metal oxide catalysts show high activity at the lower space velocity. For example, the toluene combustion on $La_{0.8}Sr_{0.2}CoO_3$ perovskite catalyst was reported at a space velocity of 186 h^{-1} and a partial pressure of toluene 192 Pa [27], and the effect of GHSV on the conversion in the combustion of toluene and methyl ethyl ketone on Cr-doped zirconia was investigated at a space velocity of 10–400 h^{-1} [21]; whereas in this report, the Cu-Mn/MCM-41 mesoporous catalyst show a high activity at about 100 times higher space velocity, e.g., 18,000–72,000 h^{-1}, which probably related with its high specific surface area, i.e., 1043 m^2/g [23] and its regular pore structure as shown in Fig. 1. From a practical point of view, the results therefore indicate that the Cu-Mn/MCM-41 mesoporous catalyst is more useful catalyst for abatement of toluene at a high space velocity.

4. Conclusion

In conclusion, the paper reports the results of experimental investigation of catalytic combustion of toluene as a model of VOCs on Cu-Mn/MCM-41 catalyst. It is found that the catalytic behavior of Cu-Mn/MCM-41 in the desired reaction is greatly affected by calcination temperature from 300 to 800 °C during the catalyst pre-treatment. The temperature of maximal catalyst activity in toluene combustion is shifted to the higher reaction temperatures with an increase in calcination temperature; however, the activity of toluene conversion remained high even after calcinations of the Cu-Mn/MCM-41 catalyst up to 800 °C, i.e., 95.4% at 360 °C, indicating that the Cu-Mn/MCM-41 catalyst is relatively thermally stable. Obviously, the calcination temperature leads to the sintering of the catalyst and influences the redox properties responsible for catalytic activity of Cu-Mn/MCM-41 catalyst in toluene combustion. Therefore, calcination temperature should be carefully optimized to prepare the catalyst with high activity.

The influence of different reaction conditions on toluene conversion is examined and discussed. The results show that an increase in toluene concentration from 3500 to 20,000 ppm leads to a decrease in the activity; toluene combustion activity was increased with an increase in oxygen concentration from 1.5 to 18.3% in the feed gas investigated here; toluene conversion remained almost unchanged for the space velocity from 18,000 to 36,000 h^{-1}, and decreased when further increasing the space velocity to 72,000 h^{-1}. Keeping in mind the previous report [23], the Cu-Mn/MCM-41 mesoporous catalyst showed the highest catalytic activity as compared to microporous catalysts and supported porous silica and the less amount of coke formation. By considering the results reported here, it is found that Cu-Mn/MCM-41 are promising catalysts for catalytic combustion of toluene in a wide range of toluene concentrations and a high space velocity, especially at lower reaction temperature.

Acknowledgements

W.B.L. thanks the Natural Science Foundation of China (no. 20277023) for partial financial support and the Royal Society from the UK for a research fellowship.

References

[1] J.J. Spivey, Ind. Eng. Chem. Res. 26 (1987) 2165.

[2] J. Carpentier, J.F. Lemonier, S. Siffert, H. Laversin, A. Aboukais, Appl. Catal. A: Gen. 234 (2002) 91–101.

[3] M. Paulis, L.M. Gandia, A. Gil, J. Sambeth, J.A. Odriozola, M. Montes, Appl. Catal. B: Environ. 26 (2000) 37–46.

[4] K. Okumura, T. Kobayashi, H. Tanaka, M. Niwa, Appl. Catal. B: Environ. 44 (2003) 325–331.

[5] K. Okumura, H. Tanaka, M. Niwa, Catal. Lett. 58 (1999) 43–45.

[6] T. Takeguchi, S. Aoyama, J. Ueda, R. Kikuchi, K. Eguchi, Topics Catal. 23 (1–4) (2003) 159–162.

[7] F.J. Maldonado-Hodar, C. Moreno-Castilla, A.F. Perez-Cadenas, Appl. Catal. B: Environ. 54 (4) (2004) 217–224.

[8] S. Ordóñez, L. Bello, H. Sastre, R. Rosal, F.V. Diez, Appl. Catal. B: Environ. 38 (2002) 139–149.

[9] M. Paulis, H. Peyrard, M. Montes, J. Catal. 199 (2001) 30–40.

[10] A.P. Antunes, M.F. Ribeiro, J.M. Silva, F.R. Ribeiro, P. Magnoux, M. Guisnet, Appl. Catal. B: Environ. 33 (2001) 149–164.

[11] F. Kovanda, K. Jiratova, J. Rymes, D. Kolousek, Appl. Clay Sci. 18 (1–2) (2001) 71–80.

[12] P.-O. Larsson, A. Andersson, L.R. Wallenberg, B. Svensson, J. Catal. 163 (1996) 279–293.

[13] D. Klissurski, E. Uzunova, K. Yankova, Appl. Catal. A: Gen. 95 (1993) 103–115.

[14] S. Scirè, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, Appl. Catal. B: Environ. 40 (2003) 43–49.

[15] S. Minicò, S. Scirè, C. Crisafulli, S. Galvagno, Appl. Catal. B: Environ. 34 (2001) 277–285.

[16] S.H. Taylor, C.S. Heneghan, G.J. Hutchings, I.D. Hudson, Catal. Today 59 (2000) 249–259.

[17] O.R. Evans, A.T. Bell, T.D. Tilley, J. Catal. 226 (2004) 292–300.

[18] J. Carpentier, J.F. Lamonier, S. Siffert, H. Laversin, A. Aboukais, Stud. Surf. Sci. Catal. 142 (2002) 1197–1204.

[19] W.B. Li, W.B. Chu, M. Zhuang, J. Hua, Catal. Today 93 (2004) 205–209.

[20] V.R. Choudhary, G.M. Deshmukh, D.P. Mishra, Energy Fuels 19 (2005) 54–63.

[21] V.R. Choudhary, G.M. Deshmukh, S.G. Pataskar, Catal. Commun. 5 (2004) 115–119.

[22] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.

[23] W.B. Li, M. Zhuang, T.C. Xiao, M.L.H. Green, J. Phys. Chem. B 110 (2006) 21568–21571.

[24] W.B. Li, Y. Zhang, Y. Lin, X. Yang, Stud. Surf. Sci. Catal. 141 (2002) 503–510.

[25] S.C. Kim, J. Hazard. Mater. B91 (2002) 285–299.

[26] H.L. Tidahy, S. Siffert, L.J.-F. Amonier, E.A. Zhilinskaya, A. Aboukais, Z.-Y. Yuan, A. Vantomme, B.-L. Su, X. Canet, G. De Weireld, M. Frere, T.B. N'Guyen, J.-M. Giraudon, G. Leclercq, Appl. Catal. A: Gen. 310 (2006) 61–69.

[27] S. Irusta, M.P. Pina, M. Menendez, J. Santamaria, J. Catal. 179 (1998) 400–412.