Catal Lett (2008) 126:106–111
DOI 10.1007/s10562-008-9588-0

Perovskite-type Oxide $LaMnO_3$: An Efficient and Recyclable Heterogeneous Catalyst for the Wet Aerobic Oxidation of Lignin to Aromatic Aldehydes

**Haibo Deng · Lu Lin · Yong Sun · Chunsheng Pang · Junping Zhuang ·
Pingkai Ouyang · Zhenjiang Li · Shijie Liu**

Received: 14 May 2008 / Accepted: 10 July 2008 / Published online: 2 August 2008

Abstract The perovskite-type oxide catalyst $LaMnO_3$ prepared by the sol–gel method was found to be an efficient heterogeneous and recyclable catalyst for the wet aerobic oxidation of lignin to aromatic aldehydes. The lignin conversion rate and the yield of each aromatic aldehyde were enhanced significantly by the catalytic process as compared with the non-catalyzed process. Moreover, the activity, specific surface area and perovskite-type structure of the $LaMnO_3$ catalyst remained nearly unchanged after five successive recycles of catalytic reactions.

Keywords Perovskite-type oxide $LaMnO_3$ · Catalytic wet aerobic oxidation · Lignin · Aromatic aldehydes · Activity · Reusability

1 Introduction

As petroleum reserves gradually decrease, the exploration of feasible pathways for the conversion of abundant and renewable biomass into clean fuels and high value-added chemicals to supplement or gradually replace the petroleum-based chemicals is highly desirable [1]. Lignocellulosic biomass is an important bioresource, consisting of three main components: cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses are the source of substrates for biological conversion into bio-ethanol; however, lignin in the biorefinery process is usually discarded as non-cellulosic wastes. The biggest barrier to the biorefinery of lignocellulosic biomass is how to convert all its total components into biofuels and/or bio-based chemicals in an economical and environmental manner [2]. One way to add economic value to the bio-refinery process is to turn the waste component, lignin, into fine chemicals. Lignin is an extremely complex three-dimensional macromolecule with irregular structure, which results from random dehydrogenation polymerization of phenyl propane building units (coniferylic, sinapylic and *p*-coumarylic alcohols, as shown in Fig. 1. in the presence of peroxidase enzymes [3]. Aromatic aldehydes such as vanillin, syringaldehyde and *p*-hydroxybenzaldehyde as shown in Fig. 2 can be obtained from the wet aerobic oxidation (WAO) process of lignin. These aldehydes have wide applications such as flavoring, chemical intermediaries for pharmaceutical drugs and agricultural defensives [4, 5].

The catalytic wet aerobic oxidation (CWAO) process using oxygen and catalysts was indicated to be an attractive procedure for the WAO of lignin to increase the yields of aldehydes. Noble metal catalyst [5–7] were extensively studied for the CWAO process of lignin. However, noble metals are expensive, greatly affecting the economics of their potential commercial applications. Alternatively, inexpensive ions of metals such as iron, copper, and cobalt have been shown to possess activity in the lignin oxidation process [8–12]. Cupric sulfate is widely researched because

H. Deng · L. Lin (✉) · Y. Sun · C. Pang · J. Zhuang
State Key Laboratory of Pulp and Paper Engineering,
South China University of Technology, Guangzhou 510640,
Guangdong Province, China
e-mail: lclulin@scut.edu.cn

H. Deng
e-mail: denghb1979@163.com

P. Ouyang · Z. Li
College of Medicine and Life Science, Nanjing University
of Technology, Nanjing, Jiangsu Province 210009, China

S. Liu
Department of Paper and Bioprocess Engineering, State
University of New York College of Environmental Science
and Forestry, 1 Forestry Drive, Syracuse, NY 13210, USA

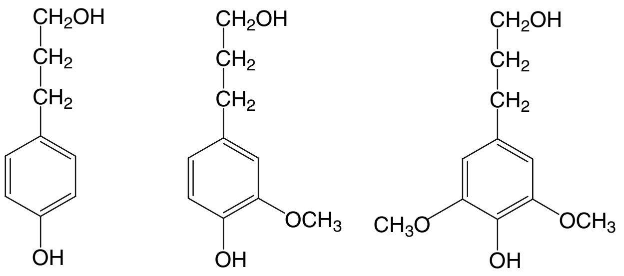
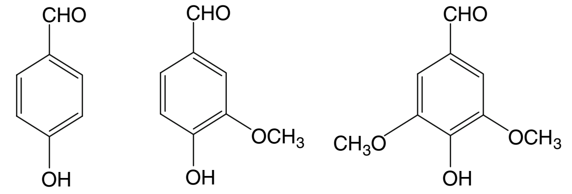


Fig. 1 Lignin building units



p-Hydroxybenzaldehyde Vanillin Syringadehyde

Fig. 2 Aromatic aldehydes from the CWAO process of lignin

it is the most effective catalyst among these chemical agents. Nevertheless, homogeneous catalysts of cupric sulfate may lead to secondary pollution, resulting in high costs if it is to be recycled. It is thus restricted in utilization in industrial applications. Therefore, the exploration for novel heterogeneous catalysts with effective and environmental benign potential that can be reused and recycled is of great significance to the biorefinery conversion of lignin to high value-added chemicals.

Recently, studies of manganese oxide as catalyst in the CWAO process have received significant attention [13–15]. Moreover, Mn(II) iron solution [16], Mn(III)- substituted polyoxometalates [3] and Mn(IV) complex [17, 18] are known to show interesting activities in the oxygen delignification of the bleaching process of pulps. On the other hand, it is well known that ABO_3 perovskite-type oxides, including $LaMnO_3$, show high activity and stability in the hydrocarbon catalytic oxidation process, which is a promising alternative to noble metal catalysts for the wet process of hydrocarbon catalytic oxidation [19–23]. Nevertheless, the activity of perovskite-type oxides in the wet aerobic oxidation reaction has rarely been studied. To the best of our knowledge, only two recent studies deal with the activity of perovskite-type oxides for the wet air oxidation reaction [24, 25], both claiming that the perovskite-type oxides presented high activity for this reaction. The objective of this paper is to study the perovskite-type oxide $LaMnO_3$ as catalyst in the catalytic wet aerobic oxidation of lignin.

2 Experimental

2.1 Lignin and Catalyst Preparation

Lignin was obtained through the enzymatic hydrolysis process of steam-explosive cornstalk [26]. The $LaMnO_3$ catalyst was prepared from citrate precursors [27]; a concentrated solution of metal nitrates was mixed with an aqueous solution of citric acid, fixing the molar ratio of citric acid to the metal cations at unity. Water was evaporated from the solution at 80 °C until a viscous gel was obtained. The gel was kept at 100 °C overnight, ground and finally calcined at 800 °C for 6 h.

2.2 Catalyst Characterization

The specific surface area of the catalyst was evaluated by N_2 adsorption at 77 K according to the Brunauer-Emmett-Teller (BET) equation using a Micromeretics ASAP 2010 instrument.

X-ray diffraction (XRD) measurements were performed on a Rigaku powder diffractometer (Rigaku, Japan) with CuK_α radiation. The tube voltage was 45 kV, and the current was 40 mA. The XRD diffraction patterns were taken over 2 h in a range of 20° to 80° at a scan speed of 2°/min.

Temperature programmed reduction (TPR) of H_2 was performed in a Micromeritics Autochem 2910 equipped with a thermal conductivity detector (TCD). After pretreatment in 10% O_2/He flow at 800 °C for 30 min, the sample (50 mg) was reduced with 5% H_2/Ar (30 cm^3/min) heating 5 °C/min from room temperature to 850 °C.

The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra system with 0.1 eV per step for detail scan and the binding energies for each spectrum were calibrated with a C1s spectrum of 284.6 eV. The core levels of Mn 2p and O1s species were recorded and their relative intensities determined.

2.3 Activity Measurements

The non-catalyzed wet aerobic oxidative (WAO) and catalyzed wet aerobic oxidative (CWAO) processes of lignin were carried out in a high-pressure SS-316 Parr slurry reactor (model 4843) at 120 ± 1 °C. The 500 mL alkaline solutions (NaOH, 2 mol/L) of lignin dissolved at a concentration of 60 g/L were introduced into the reactor and a certain quantity of catalysts was added to the solution if necessary. The heating program was started under a slight nitrogen pressure. When the solution in the reactor reached the desired temperature, nitrogen was added until a total pressure of 15 bars was attained. Time was recorded from zero, corresponding to the admission of oxygen, to a total pressure of 20 bars. The total pressure in the reactor was kept at 20 bars by continuous flushing of oxygen for supplement because of its consumption during the reaction. During reactions, sampling was conducted from the reactor to detect changes of reactant lignin and any aromatic aldehydes produced. After filtration, liquid samples obtained were acidified to pH 2–3 with an HCl solution. Acidification led to the precipitation of high molecular weight components, including aromatic aldehydes and lignin that was not converted. The resulting products were extracted with chloroform until the chloroform layer appeared colorless. The residual lignin was obtained by centrifugation of the suspensions after the extraction of resulted products.

The compositions of the extraction from the chloroform were analyzed by high performance liquid chromatography equipped with a Hypersil ODS2 column (4.6 mm × 250 mm) and a UV detector at 280 nm to quantitatively determine the contents of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. A mixture of acetonitrile (10%), deionized water (90%) and acetic acid (1.5%) was used as the mobile phase. The non-converted lignin was diluted in a 2 N solution of sodium hydroxide in order to dissolve the lignin. The amount of lignin was measured by UV spectrophotometer at a wavelength of 280 nm [28].

The experiment to test the recycling ability of $LaMnO_3$ was performed as follows. Fresh catalyst and lignin solution were added into the reactor and the process was performed under the same conditions as mentioned above for 30 min. After the CWAO reaction, the reactor temperature was quickly cooled to room temperature, and the resulting products were carefully poured out and then filtered, while the catalyst was left in the reactor. Fresh lignin solution was then added and the process was performed again under the same conditions for 30 minutes. This procedure was repeated four times. The treatment of samples and quantitative analysis were the same as above.

3 Result and Discussion

3.1 Surface Oxygen Species and Mn Ion Oxidation States

Shown in Fig. 3 are the O 1s and Mn 2p XPS spectra of the catalyst. The graphs show that the catalyst $LaMnO_3$ was a typical perovskite-type oxide. As can be seen from the O1s spectrum (Fig. 3a), two contributions were obtained by curvefitting of O1s: 528.9 and 530.6 eV, which could be assigned to lattice oxygen in the form of O^{2-} (metal oxygen bond) and adsorbed oxygen species (such as O^{-}, O_2^{-}, or O_2^{2-}), respectively [29, 30]. From Fig. 3b, one can observe the appearance of two signals at BE = 641.6 and 653.6 eV, assignable to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively [31, 32]. The asymmetry of the two peaks indicates the existence of mixed components: the former could be resolved into two components at BE = 640.8 and 642.3 eV, whereas the latter into the ones at BE = 652.5 and 653.8 eV. The signals at BE = 640.8 and 652.5 eV are attributable to Mn^{3+} ions, and the ones at BE = 642.3 and 653.8 eV to Mn^{4+} ions [31, 32].

3.2 Reducibility of the Catalyst

To investigate the reducibility of $LaMnO_3$ samples, an H_2-TPR test was performed and the result was plotted in Fig. 4. The TPR profile of $LaMnO_3$ presents the typical structure of perovskite-type $LaMnO_3$, giving rise to two main peaks: the first with a maximum at approximately 460−470 °C and second at the maximum temperature of the analysis at 850 °C. According to the literature cited, the first peak in the literature is attributed to the reduction of Mn^{4+} to Mn^{3+} and the second to the reduction of Mn^{3+} to Mn^{2+} [33], the latter having not completed yet at 850 °C.

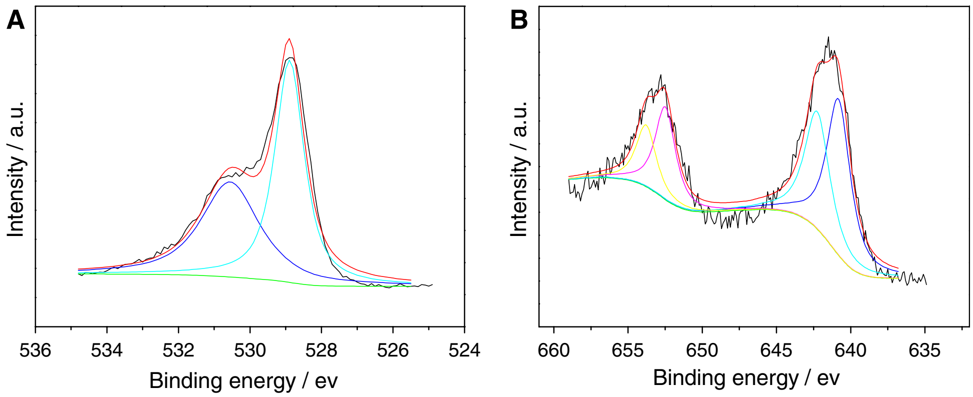


Fig. 3 (**a**) O1s and (**b**) Mn 2p XPS spectra of $LaMnO_3$

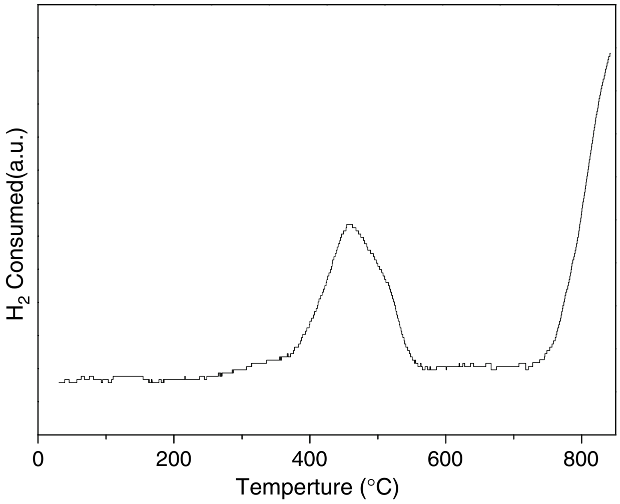


Fig. 4 TPR profile of the $LaMnO_3$ catalyst

3.3 Catalytic Activity

The aromatic aldehydes, the oxidative products from lignin in the CWAO process, can be further oxidized to aromatic acids, and even to carbon dioxide and water under certain conditions. In our experiment, the catalytic activity was evaluated in comparison with the results of each case indicated as the rate of lignin conversion and the yield of aldehydes. Rate of lignin conversion and yield of each aromatic aldehyde were significantly higher with the catalyst $LaMnO_3$ than that without the catalyst (Fig. 5). In the absence of a catalyst, the lignin conversion was 41.8% at 3.0 hours (Fig. 5a). When $LaMnO_3$ was used, the lignin conversion was 57.0% after 3 hours, 1.36 times that obtained in the noncatalytic process. The maximum yield of *p*-hydroxybenzyl aldehyde was 2.032% in 120 minutes with the $LaMnO_3$ catalyst, 31.3% higher than that of the noncatalytic process, whose maximum yield was 1.548% at 150 minutes (Fig. 5b). The maximum yields of vanillin and syringaldehyde were 4.321% (30 min) and 9.326% (30 min) in the $LaMnO_3$ catalytic process, 1.37 and 1.96 times those obtained in the noncatalytic process, respectively (Fig. 5c and d).

The same concentration of $LaCl_3$ ion solution as that of $LaMnO_3$ did not present any catalytic activity under these conditions, while an equivalent concentration of $MnSO_4$ presented modest catalytic activity under these conditions compared to that under the non-catalyst process (Fig. 5a–d). Thus, it is concluded that only the manganese was active for the lignin oxidation reaction, since the redox reaction of manganese happens in the presence of oxygen; while for the inert lanthanum, no redox reaction could take place, because it has only one stable valence, the +3 state. Nevertheless, it was interesting to note that the activity of the Mn^{2+} was less inactive for the oxidation reaction than that in the $LaMnO_3$ catalytic process under the same conditions (Fig. 5a–d). The results imply that manganese salts are not a viable option in the CWAO process of lignin compared to $LaMnO_3$, due to its poor catalytic activity.

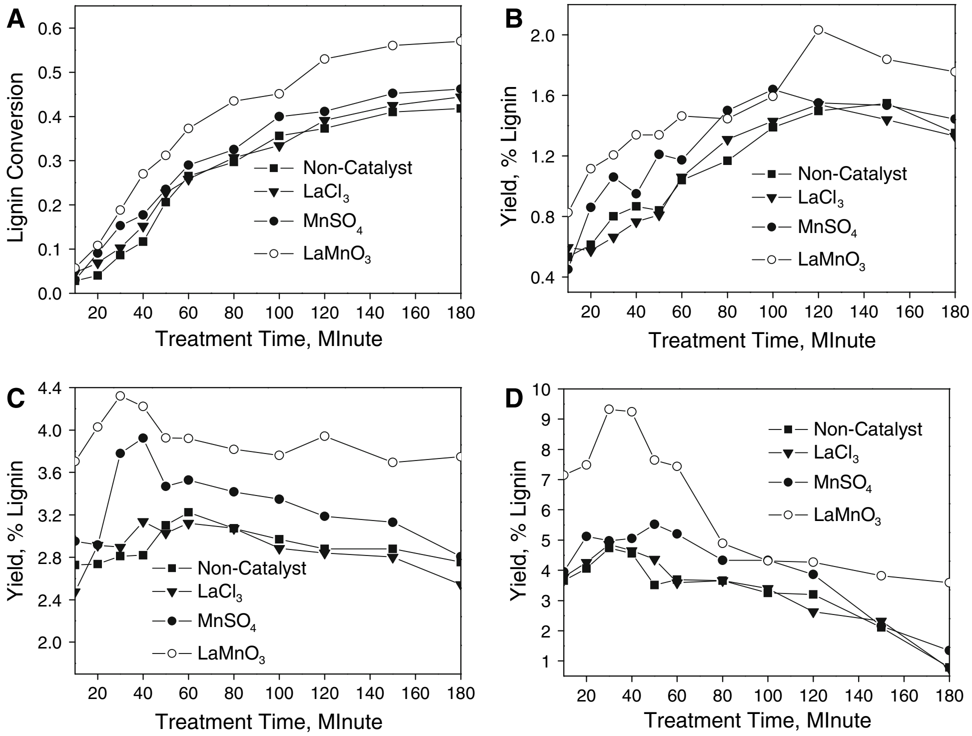


Fig. 5 Lignin conversion (**a**), yield of *p*-hydroxybenzaldehyde (**b**), vanillin (**c**) and syringaldehyde (**d**) with reaction time. The reaction conditions were as follows: NaOH (2 mol/L), 120 °C, 5 bar partial pressure of oxygen in 20 bar total pressure, $CL_0 = 60.00\ kg/m^3$ in comparison to non-catalyzed process (■), 5% (W/W, on lignin) $LaCl_3$ (▲), $MnSO_4$ (●), $LaMnO_3$ (○) as catalyst in catalytic process, and the lignin conversion = $(C_0 - C_t)/C_0$, where C_0 is the initial concentration of lignin, and C_t is the concentration of lignin at any reaction time

Although it is premature to discuss the precise role of the perovskite oxide $LaMnO_3$ in the catalytic mechanism of the lignin oxidation process at present, it is noteworthy that two aspects can account for the activity of $LaMnO_3$ in the CWAO as reported [24]: the first involving the Mn^{4+}/Mn^{3+} redox couples, the second contributing to chemisorbed oxygen on the perovskite surface under the controlled temperature, resulting from oxygen molecules dissolved in the reaction solution. As it is well known that the states of $LaMnO_3$ are beneficial to the catalytic wet air oxidation (CWAO) process, the existence of Mn^{4+} was confirmed by Mn 2p XPS spectra and the TPR profile of the catalyst in the study; nevertheless, the detailed mechanisms of $LaMnO_3$ in the CWAO process of lignin need to be explored in future experiments.

3.4 Catalyst Stability

In order to examine the possible reusability of the catalyst $LaMnO_3$ under these reaction conditions, repeated use of the catalyst $LaMnO_3$ has been carried out. Fig. 6 shows the lignin conversion and yield of aromatic aldehydes from the non-catalyzed process and five successive reuses of the catalyst. The lignin conversion and the yield of each aromatic aldehyde were significantly higher in each of five successive catalyst reuses than those of the non-catalyzed process. Furthermore, the results clearly demonstrated that the lignin conversion and the yield of aromatic aldehydes remained nearly the same in each reuses (Fig. 6) and the small differences measured for all the samples are within instrumental error, indicating that the catalyst can be reused at least 5 times.

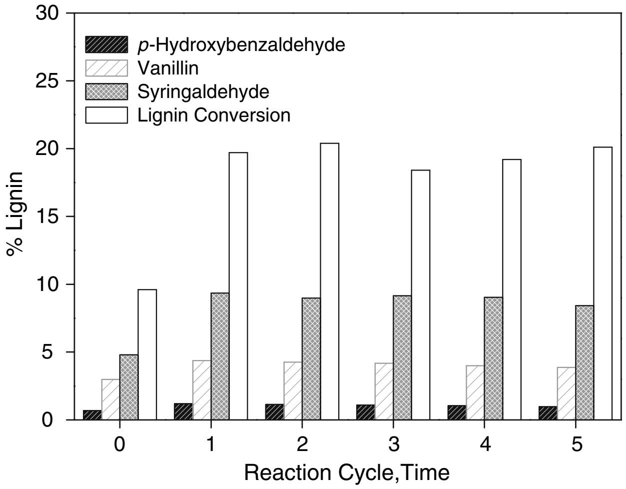


Fig. 6 Lignin conversion and yield of aromatic aldehydes in the absence of catalyst (process 0) and five successive uses of the catalyst with each time for 30 min. The other reaction conditions are as in Fig. 1

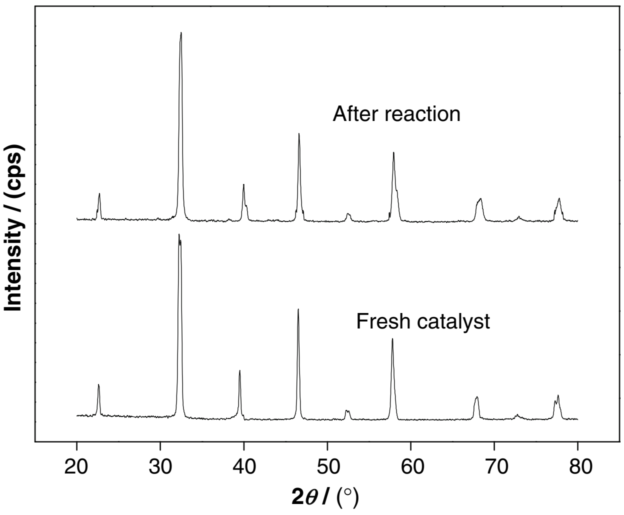


Fig. 7 XRD patterns of the fresh catalyst and the catalyst after five successive reuses

The crystalline phases of the catalysts before and after the five successive uses were also determined by X-ray diffraction (Fig. 7). The XRD patterns of the $LaMnO_3$ catalyst before the reaction and after the five successive uses all showed characteristic reflections for the perovskite-type oxide without other phases. No obvious changes can be seen in the structure of the $LaMnO_3$ catalyst after the fifth run, suggesting that the $LaMnO_3$ catalyst in the CWAO process was stable. It was observed that the specific surface area of the fresh $LaMnO_3$ catalyst and those after five successive uses remained nearly unchanged, at 21.4 and 20.8 m^2/g, respectively, within instrumental error. These results indicate that the active phase of catalyst $LaMnO_3$ itself was not deactivated under the conversion conditions, which is closely related to the reusability of the $LaMnO_3$ in the CWAO process of lignin. The high activity and reusability of the perovskite-type oxide catalyst $LaMnO_3$ presents a bright prospect for the conversion of lignin to high value-added aromatic aldehydes.

4 Conclusion

The perovskite-type oxide $LaMnO_3$ catalyst prepared by the sol–gel method exhibited high activity in the CWAO of lignin. Rate of lignin conversion and yield of each aromatic aldehyde were improved significantly in the $LaMnO_3$ catalyst process, compared to the non-catalyzed process. The $MnSO_4$ catalyst presented modest catalytic activity as compared to the high activity of the $LaMnO_3$ catalyst in the CWAO of lignin, indicating that manganese salts are not a viable option in the CWAO process of lignin. The perovskite-type oxide catalyst $LaMnO_3$ also possesses distinctive stability of activity and structure in the CWAO of lignin.

Thus, the perovskite-type oxide $LaMnO_3$ is an efficient and recyclable heterogeneous catalyst for the conversion of lignin in the CWAO process of lignin.

Acknowledgements The authors are grateful to the financial support from Natural Science Foundation of China (50776035, U0733001), Foundation of Scientific Research for Universities(20070561038) and Initiative Group Research Project(IRT0552) from Ministry of Education of China, National High Technology Project (863 project) (2007AA05Z408) and National Key R&D Program (2007BAD34B01) from the Ministry of Science and Technology of China.

References

1. Rostrup-Nielsen JR (2005) Science 308:1421
2. Eckert C, Liotta C, Ragauskas A, Hallett J, Kitchens C, Hillac E, Draucker L (2007) Green Chem 9:545
3. Gaspar A, Evtuguin DV, Pascoal Neto C (2003) Appl Catal A Gen 239:157
4. Sridhar P, Araujo JD, Rodrigues AE (2005) Catal Today 105:574
5. Sales FG, Maranhão LCA, Filho NML, Abreu CAM (2006) Ind Eng Chem Res 45:6627
6. Sales FG, Abreu CAM, Pereira JAFR (2004) Braz J Chem Eng 21:211
7. Sales FG, Maranhão LCA, Filho NML, Abreu CAM (2007) Chem Eng Sci 62:5386
8. Mathias AL, Rodrigues AE (1994) Holzforscung 49:273
9. Wu GX, Heitz M, Chornet E (1994) Ind Eng Chem Res 33:718
10. Wu GX, Heitz M (1995) J Wood Chem Technol 15:189
11. Tarabanko VE, Petukhov DV, Selyutin GE (2004) Kinet Catal 45:603
12. Villar JC, Caperos A, García-Ochoa F (2001) Wood Sci Technol 35:245
13. Su Y, Wang LC, Liu YM, Cao Y, He HY, Fan KN (2007) Catal Commun 8:2181
14. Hu J, Sun KQ, He DP, Xu BQ (2007) Chin J Catal 28:1025
15. Santiago AFJ, Sousa JF, Guedes RC, JerÔnimo CEM, Benachour M (2006) J Hazard Mater 138:325
16. Landucci LL, Sanyer N (1975) Tappi 58:60
17. Cui Y, Chen CL, Gratzl JS, Patt R (1999) J Mol Catal A Chem 144:411
18. Alves V, Capanema E, Chen CL, Gratzl J (2003) J Mol Catal A Chem 206:37
19. Seiyama T (1993) In: Tejuca LG, Fierro JLG (eds) Properties and applications of perovskite-type oxides. Marcel Dekker, New York, p 215
20. Nitadori T, Ichiki T, Misono M (1988) Bull Chem Soc Jpn 61:621
21. Yamazoe N, Teraoka Y (1990) Catal Today 8:175
22. Szabo V, Bassir M, Van Neste A, Kaliaguine S (2002) Appl Catal B 37:175
23. Zhang RD, Villanueva A, Alamdari H, Kaliaguine S (2006) Appl Catal A Gen 307:85
24. Yang M, Xu AH, Du HZ, Sun CL, Li C (2008) J Hazard Mater 139:86
25. Royer S, Levasseur B, Alamdari H, Barbier J, Duprez D, Kaliaguine S (2007) Appl Catal B Env 80:51
26. Bentivengaa G, Boninib C, Auriab MD, Bonaa AD (2003) Biomass Bioenergy 24:233
27. Barnabé A, Gaudon M, Bernard C, Laberty C, Durand B (2004) Mater Res Bull 39:725
28. Žabková M, Borges EAS, Rodrigues AE (2007) J Membr Sci 301:221
29. Carley AF, Roberts MW, Santra AK (1997) J Phys Chem B 101:9978
30. Fierro JLG, Tejuca LG (1987) Appl Surf Sci 27:453
31. Carver JC, Schweitzer GK (1972) J Chem Phys 57:973
32. Niu JR, Deng JG, Liu W, Zhang L, Wang GZ, Dai HX, He H, Zi XH (2007) Catal Today 126:420
33. Svensson EE, Nassos S, Boutonnet M, Järås SG (2006) Catal Today 117:484