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EFFECT OF CALCINATION TEMPERATURE ON MANGANESE OXIDE-ACTIVATED CARBON FOR CATALYTIC OXIDATION OF BENZYL ALCOHOL

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ABSTRACT

Mn_3O_4/AC catalysts were synthesized by deposition-precipitation method and calcined at different temperature. The effects of calcination temperature on the physicochemical properties of the catalysts were assessed by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). It was found that all the catalysts were composed solely of Mn_3O_4 in the calcination temperature range of 450°C to 550°C. The catalytic performance of the catalyst for the selective oxidation of benzyl alcohol with hydrogen peroxide as oxidant was subsequently examined. Mn_3O_4/AC-450 catalyst exhibited the highest catalytic activity at 63.8% conversion of benzyl alcohol under mild conditions. Crystallite size and dispersion of catalysts due to the different calcination temperature have significant role in the catalytic process.

Keywords: manganese oxide; activated carbon; benzyl alcohol; oxidation

INTRODUCTION

The oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) is an industrially important reaction due to its wide applications in perfumery and pharmaceutical industries [1]. Transition metal based heterogeneous catalysts has attracted increasing interest due to the inexpensive nature and tunability. Manganese oxides is one of the most used transition metal oxides catalyst due to highly efficient redox properties [2]. Recently, manganese oxides have been extensively studied in the aerobic oxidation of alcohols and exhibited high catalytic activity and selectivity [3]. It was reported that manganese containing octahedral molecular sieves with tunnel or layer structures selectively oxidize BzOH to BzH in the presence of oxygen [4,5]. Yang et al. demonstrated that Mn confined in carbon nanotubes K-birnessite showed excellent selectivity (above 99%) towards BzH [6].

There are many factors that contribute to the performance of manganese oxide catalysts.

The influence of calcination temperature of precursors on the physiochemical property and catalytic activity of the final products should be addressed. The crystallinity and particle dispersion formed during different calcination temperature will have effects on the catalytic activity. Calcination temperature also determines the final oxidation state of the supported manganese [7,8] which will then determine the metal dispersion [9]. Thus, it is important to investigate various calcination temperature to optimize the performance of the catalyst.

Activated carbon (AC) supported catalysts hold several advantages compared to silica and alumina-supported catalysts. Interaction between support and active component is minimized due to the inert graphitic surface, which leads to an optimized utilization of active sites [10,11]. In addition, immobilizing active species onto supports could effectively reduce the aggregation of nanoparticles due to their small particle size [12].
In this paper, deposition-precipitation method was employed to anchor Mn_3O_4 uniformly on AC under different calcination temperature. Their catalytic performance has been addressed by the oxidation of benzyl alcohol to benzaldehyde using hydrogen peroxide as oxidant. The correlation among calcination temperature, structure, and catalysis has been formulated based on the characterization and experimental results.

EXPERIMENTAL

Preparation of Mn_3O_4/AC

The Mn_3O_4/AC were prepared by using homogeneous deposition-precipitation method previously reported with slight modification [13]. In brief, 1.0 g of AC was added into 50 mL aqueous solution of 0.1 mol of $Mn(NO_3)_2.4H_2O$ under stirring at room temperature. The resulting mixture was stirred for 15 min and 0.1 mol L^{-1} of NaOH was added dropwise, under vigorous stirring at room temperature until the pH becomes 10.0. The resulting solution was left at room temperature for 24 h, centrifuged and washed with deionized water until pH 7. The prepared sample was dried at 110°C overnight followed by calcination at 450°C in air for 3 h, with sample named as Mn_3O_4/AC-450. To compare the effect of calcination temperature, Mn_3O_4/AC-500 and Mn_3O_4/AC-550 were prepared by similar steps with calcination temperature of 500°C and 550°C, respectively.

Characterization of Mn_3O_4/AC

The crystalline structures were obtained by D8 Advance (BRUKER AXS, Germany) diffractometer using Cu Kα radiation (λ = 1.541 Å) from X-ray diffraction (XRD) patterns. The morphology and microstructures of the prepared samples were characterized from the Scanning Electron Microscope (SEM) images taken with JSM-6390 (JEOL, USA).

Catalytic testing of Mn_3O_4/AC

The catalytic oxidation of benzyl alcohol was carried out using procedures that was reported previously with slight modification [14] in a batch type reactor. In a typical reaction, the sample powder (0.1 g) was loaded in a 50 mL double neck round bottom flask containing a mixture of benzyl alcohol: H_2O_2 = 1:1.3 with H_2O_2 as oxidant in 20 mL toluene as solvent. The flask was connected to a reflux condenser, magnetically stirred and kept in an oil bath at 80°C for 2h. After each reaction period, the final mixture was centrifuged to remove the catalyst. The liquid phase were filtered and analysed by gas chromatography-mass spectrometry (GC-MS SHIDMADZU QP 5000) equipped with a flame ionization detector (FID) and a medium polarity capillary column (BPX-5 column 29.4 m×0.25 mm), with film thickness of 0.25μm and helium as the carrier gas to evaluate the products.

RESULTS AND DISCUSSION

Characterization of Mn_3O_4/AC

X-ray diffraction patterns which shows the crystalline nature of the Mn_3O_4/AC prepared using various calcination temperature are shown in figure 1. The weak diffraction peak at $2\theta = 26.5°$ was assigned to the activated carbon support [15] with hexagonal phase according to PDF no. 01-071-3739. The structure for AC remains the same even after modifications with Mn. The diffraction peaks of Mn_3O_4/AC are all sharp and of high intensity. The position and relative intensities of the peaks especially major peaks at 2θ and planes of 18.1 (101), 28.9 (112), 32.4 (103), 36.2 (211), 44.3 (220), 58.5 (321) and 59.8 (224) can be associated and indexed to the tetragonal phase of Mn_3O_4 [2] as of PDF no. 01-089-4837. There is no evidence of any crystal phase attributed to other oxidation state of Mn or other metal oxides, indicating the purity of the tetragonal Mn_3O_4 phase. This suggests that there is only single oxidation state of Mn.

The crystallinity of the resulting manganese oxides gradually increased upon increasing the calcination temperature as observed from the increase in the intensity of the peaks. The size of the Mn_3O_4/AC catalysts were determined from the Scherrer equation and shown in Table 1. The crystallite size increases with increasing calcination temperature. The results clearly indicated that the growth and crystallization of Mn_3O_4 had been greatly influenced by the calcination temperature.

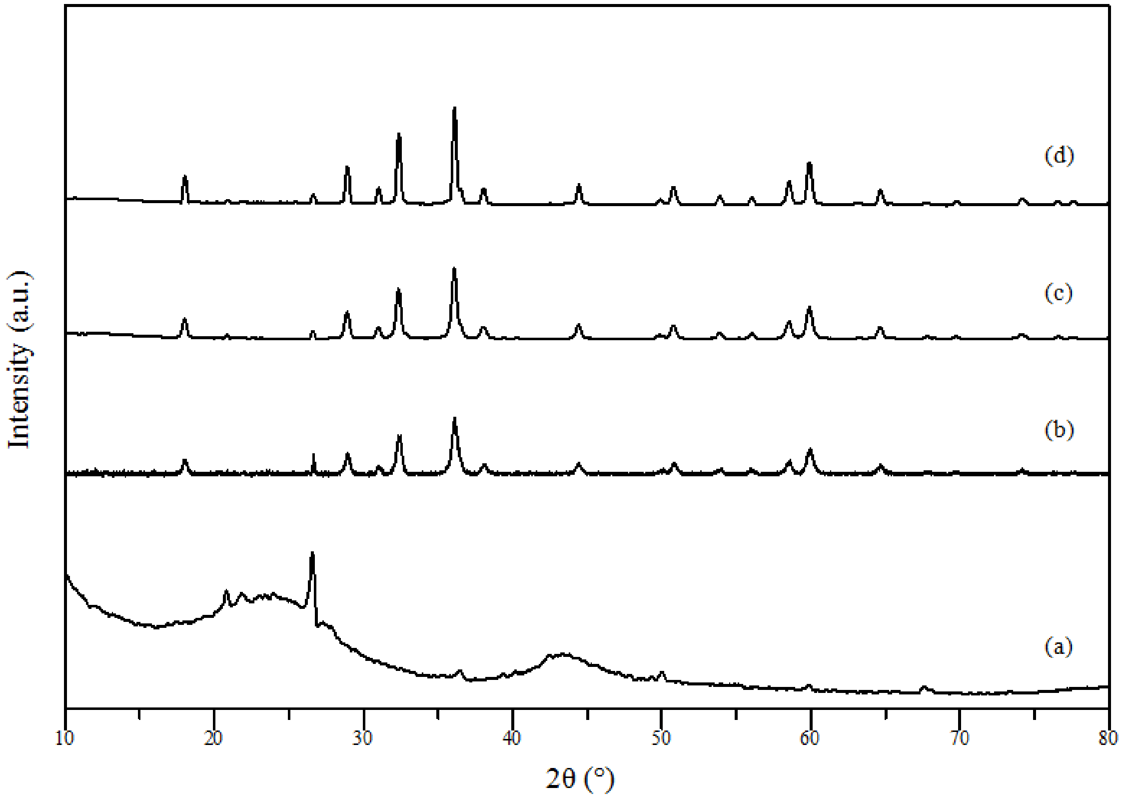

Figure 1: XRD patterns of (a) AC (b) Mn_3O_4/AC-450 (c) Mn_3O_4/AC-500 and (d) Mn_3O_4/AC-550

Table 1: Effect of calcination temperature on the catalytic performance of Mn_3O_4/AC sample[a]

Entry	Catalyst	Temperature/°C	Crystallite size/nm	Conversion/%	Selectivity/%
1	Mn_3O_4/AC -450	450	17.3	63.8	>99
2	Mn_3O_4/AC -500	500	29.5	38.3	>99
3	Mn_3O_4/AC -550	550	46.6	32.8	>99

[a]Conditions: catalyst = 0.1 g, benzyl alcohol = 25mmol, T = 353 K, H_2O_2 oxidant, t=2h.

The as-synthesized catalysts surface morphology was analyzed using SEM. SEM images of the samples calcined at different temperature was shown in figure 2. SEM images of pure AC showed that the sample had smooth surface with irregular shaped particles with fine cracks attached on its surface. As Mn was added onto AC, clusters of particles can be observed on the AC surface for all samples. When the calcination temperature was 450°C, Mn_3O_4 had an uneven surface and contained many sphere-liked and rod-liked shapes in irregular sizes ranged from 0.50 µm to 2.00 µm. Mn_3O_4/AC-500 showed uneven surface with a few pores indicating that Mn_3O_4 were distributed on the AC layer. The size of the particles ranged from 0.70 µm to 2.15 µm. Mn_3O_4/AC-550 also showed similar morphology to Mn_3O_4/AC-500. It is deduced that the morphology of the catalysts did not vary with the different calcination temperature but varied in the particle size. The particle size of Mn_3O_4/AC increased as the calcination temperature increases. The agglomeration of Mn_3O_4/AC-500 and Mn_3O_4/AC-550 samples imply that the crystallinity and aggregation of Mn_3O_4 were promoted by the rising calcination temperature as compared to Mn_3O_4/AC-450.

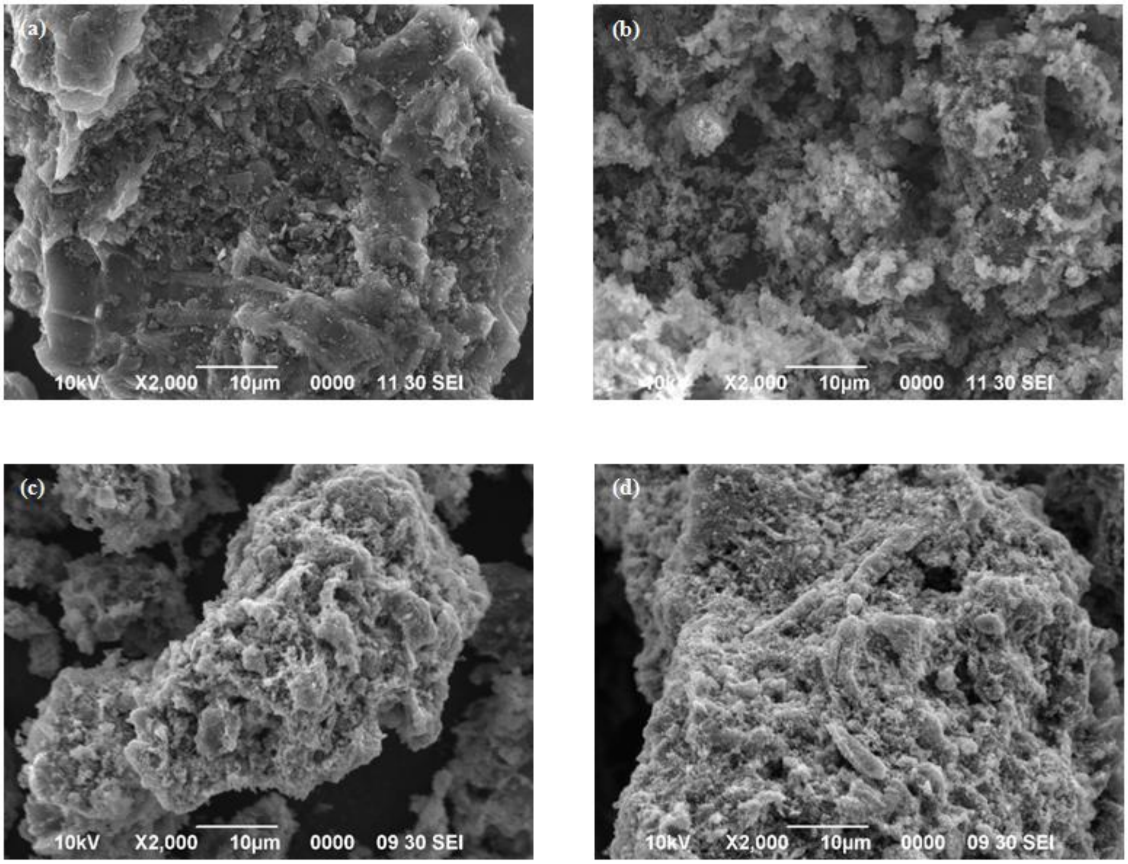

Figure 2: SEM images of (a) AC (b) Mn_3O_4/AC-450 (c) Mn_3O_4/AC-500 and (d) Mn_3O_4/AC-550

Catalytic activity

The BzOH oxidation activities of all Mn_3O_4/AC samples obtained at different calcination temperatures were studied under identical conditions using H_2O_2 as oxidant. Their catalytic performances are listed in Table 1. All prepared samples exhibited target selectivity for BzOH oxidation, with only BzH produced.

The calcination temperature evidently had a significant effect on the catalytic activity of Mn_3O_4/AC. Mn_3O_4/AC-450 showed the highest conversion at 63.8%. This result suggests that low-temperature calcination gives rise to the formation of highly active Mn species for BzOH oxidation. Mn_3O_4/AC-450 catalyst prepared showed higher activity for the selective oxidation of benzyl alcohol than MnO_x/AC with Mn^{2+} and Mn^{3+} oxidation states with H_2O_2 as oxidant [16]. Mn_3O_4 synthesized under the present conditions could generate a significant amount of O^{2-} species on the surface that contributed to the high catalytic activity in the oxidation reaction [2].

The crystallite size increased with increasing calcination temperature from 500 °C to 550 °C, leading to a lower catalytic performance. When the calcination temperature is above 450 °C, the increase agglomeration phenomenon decreases the catalytic activity. This indicates that a decrease in electron transfer due to the reduced available active sites [17]. In the oxidation reaction, reduced manganese oxide can readily be re-oxidized by dioxygen. Manganese oxide function as electron-transfer mediator to generate a rapid electron-transfer path during oxidation reactions [18] It is believed that the smaller particle size as observed from XRD and SEM for Mn_3O_4/AC-450 was beneficial to improve the catalytic activity facilitating the electron transfer. Similar trend is also observed for Au/CuO-ZrO_2 catalysts [19]. The smaller particle size may have contributed to the higher number of active sites. Although higher calcination temperature increases the crystallinity of the samples, it did not increase the catalytic activity. In this case, the number of active sites was the major factor affecting the catalytic activity.

CONCLUSIONS

The effect of calcination temperature on the physicochemical and catalytic properties of Mn_3O_4/AC catalysts prepared by deposition-precipitation method was investigated. Different calcination temperature had a significant effect on the nature of Mn_3O_4 on the surface of AC which markedly affected the catalytic conversion of benzyl alcohol. Small crystallite size and high dispersion of Mn_3O_4 were observed for Mn_3O_4/AC-450 which generate rapid electron-transfer path during oxidation reactions. These factors contributed the high catalytic performance of Mn_3O_4/AC-450 with 63.8% conversion of benzyl alcohol to benzaldehyde.

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REFERENCES

[1] Nguyen TT, Nguyen TN; *J. Sci: Adv Mat. Devices.* **3** 289 (2018)
[2] Fei J, Sun L, Zhou C, Ling H, Yan F, Zhong X, Lu, Y, Shi J, Huang J, Liu Z ; *Nanoscale Res. Lett.* **12**, 23 (2017)
[3] Hu Z, Zhao Y, Liu J, Wang J, Zhang B, Xiang X; *J. Colloid Interface Sci.* **483** 26 (2016)
[4] Son YC, Makwana VD, Howell AR, Suib SL; *Angew. Chem.***113** 4410 (2001)
[5] Makwana WD, Son YC, Howell AR, Suib SL; *J. Catal.* **210**, 46 (2002)
[6] Yang M, Ling Q, Yang H, Li C, Zhang A; *Catal. Commun.* **46**, 238 (2014)
[7] Bakker WJW, Kapteijn F, Moulijn JA; *Chem. Eng. J.* **96**, 223 (2003)
[8] Ma Y, Wang SG, Fan MH, Gong WX, Gao BY; *J. Hazard. Mater.* **168** 1140 (2009)

[9] Wang J, Qiu B, Han L, Feng G, Hu Y, Chang L, Bao W; *J. Hazard. Mater.* **213–214**, 184 (2012)
[10] Duchet JC, van Oers EM, de Beer VHJ, Prins R J.; *Catal.* **80**, 386 (1983)
[11] Li Z-R, Fu Y-L, Jiang M, Hu T-D, Liu T, Xie Y-N; *J. Catal.* **199**, 155 (2001)
[12] Shinde VM, Skupien E, Makkee M; *Catal. Sci. Technol.* **5**, 4144 (2015)
[13] Nguyen QL, Quan NA; *Reac. Kinet. Mech. Cat.* **114**, 147 (2015)
[14] Wu G, Gao Y, Ma F, Zheng B, Liu L, Sun H, Wu W; *Chem. Eng. J.* **271**, 14 (2015)
[15] Al-Marri AH, Khan M, Shaik MR, Mohri N, Adil SF, Kuniyil M, Alkhathlan HZ, Al-Warthan A, Tremel W, Tahir MN, Khan M, Siddiqui MRH; *Arabian J. Chem.* **9**, 835 (2016)
[16] Tang Q, Huang X, Chen Y, Liu T, Yang Y; *J. Mol. Catal.* **301**, 24 (2009)
[17] Zhang Q, Cheah P, Han F, Dai Q, Yan Y, Pramanik A, Ray PC; *Ceram. Int.* **45**, 21851(2019)
[18] Oishi T, Yamaguchi K, Mizuno N; *ACS Catal.* **1**, 1351 (2011)
[19] Wang Y, Yuan D, Luo J, Pu Y, Li F, Xiao F, Zhao N; *J. Colloid Interf. Sci.* **560**, 130 (2020)