

Oxidation of benzyl alcohol to benzaldehyde over MnO_x/sepiolite catalysts

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Abstract

MnO_x/sepiolite catalysts were synthesized by precipitation method accompanied by the calcination at 410°C. The prepared solids have been characterized by XRD, SEM, TPR-H₂. MnO_x particles were deposited on the surface of the sepiolite fibers and act as active sites for the oxidation of benzyl alcohol using *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent. The catalysts showed a good conversion of benzyl alcohol to benzaldehyde at 60 °C. The influence of the reaction time and reaction temperature was considered.

Keywords. MnO_x/sepiolite, oxidation, benzyl alcohol conversion, TBHP, benzaldehyde.

1. INTRODUCTION

The selective oxidation of benzyl alcohol to benzaldehyde is an important reaction in the pharmaceutical, dyestuff, agrochemical and perfume industries. For a long time ago, benzaldehyde was produced by hydrolyzing benzyl chloride or by oxidizing toluene. Product mixture from these reactions has low selectivity to desired product or contaminates chlorine causing drawbacks for environmental influence. An other way is to use homogeneous catalysts as CrO₃/H⁺ or a complex of transition metal in oxidation of benzyl alcohol that meet difficulties as the separation and recycling catalysts. Therefore, development of heterogeneous catalysts for the selective oxidation of benzyl alcohol became more attractive for many chemists. Recently, a vast number of supported noble-metal catalysts (such as Pt, Pd, Au) have exhibited very low selective oxidation of alkyl benzene at mild conditions. However, these materials are high expenditure and difficult preservation. In the present study, manganese oxide supported on sepiolite may be an alternative to noble metal as catalysts for the oxidation benzyl alcohol. Indeed, manganese was reported to be active for the alkyaromatics with *t*-BuOOH [6], but was not used for the oxidation of benzyl alcohol up to now.

Sepiolite is a clay mineral, which is a hydrated magnesium silicate, its structure consists of 2:1 units linked together by inversion SiO₄ tetrahedral along of Si-O-Si bonds; this structural arrangement

corresponds to unique framework of nanotunnels. This unique fibrous structure gives sepiolite a large specific surface area and high adsorption capacity. This is the main reason of the usage of sepiolite to obtain high dispersion of the manganese oxide species which is one of the most important factors in determining the catalytic activity and selectivity [9-16]. So in this study, the distribution of manganese species on sepiolite for the oxidation of benzyl alcohol was investigated. The preliminary results show that MnO_x/sepiolite is a promising catalyst for the oxidation of benzaldehyde.

2. EXPERIMENTAL

2.1. Catalyst preparation and characterization

The catalyst was prepared as follows: A quantity of 4 grams sepiolite was put into a 500 mL flask containing 100 mL of distilled water and desired mass ratio of manganese nitrate under stirring and then, precipitated with an excess of NaOH in 2 hours. The precipitate was separated by filtration, washed and dried at 70 °C. After that, the solid was calcined at 410 °C for 4 h, and then it was grinded.

The crystalline structure was investigated by X-ray diffraction (XRD) on a D8 Advance-Bruker instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Scanning Electron Microscopy was recorded on Hitachi S-4500 (Japan) with the magnification of 200,000 times. Temperature programmed reduction (TPR) measurements in the range of 20-800 °C were

carried out on Thermal conductivity detector Gow-Mac 69-350 with the heat rate of $10^{\circ}\text{C}/\text{min}$.

2.2. Catalytic performance

Liquid phase oxidation of benzyl alcohol (BA) has been carried out in a 100 mL three-neck glass flask fitted with a reflux condenser and a thermometer, 3 ml of benzyl alcohol and 0.2 grams of catalyst were added into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, *tert*-butyl hydroperoxide solution (TBHP, 70 %) was dropped into stirred reaction mixture and the reaction is initiated. The three-neck glass flask was cooled to room temperature and then catalyst was separated by filtration. The filtrate was quantitatively analyzed by a gas chromatography (GC-MS, HP-6890 Plus). The conversion was calculated as the follows:

$$\text{Conversion}(\%) = \frac{[\text{Alcohol}]_{\text{initial}} - [\text{Alcohol}]_{\text{final}}}{[\text{Alcohol}]_{\text{initial}}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

3.1.1. XRD patterns

Figure 1 shows the XRD diagram of sepiolite and $\text{MnO}_x/\text{sepiolite}$ (calcined at 410°C). In which, $2\theta = 7.4, 20.2, 28.5, 39.2^{\circ}$ are the characteristic peaks for sepiolite while the values of $2\theta = 32.8, 36.0, 50.9^{\circ}$ are essentially characteristic peaks for Mn_3O_4 phase, indicating the presence of Mn_3O_4 oxide on the carrier [8, 9, 13, 16, 17].

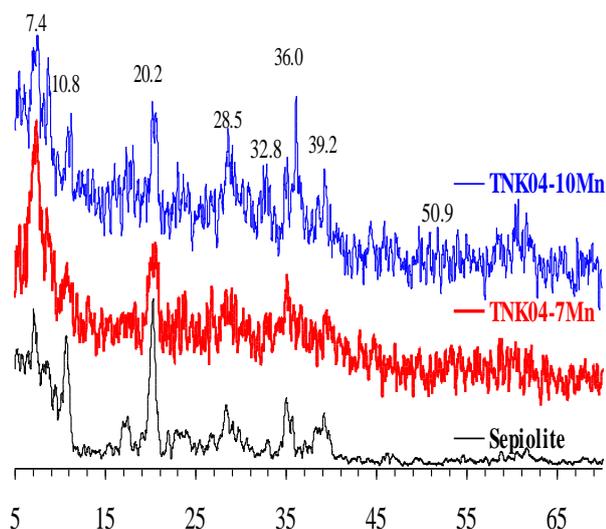


Figure 1: X-ray diffraction patterns of sepiolite, TNK04-7Mn, and TNK04-10Mn

It is noted that the intensity of the latter reflection signals disappear for the lower Mn-content sample (TNM-4-7Mn) due to the high dispersion of manganese oxide particles on the sepiolite matrix.

3.1.2. SEM and specific surface area

The SEM of sepiolite and 10 wt.% $\text{Mn}^{2+}/\text{sepiolite}$ (TNK04-10Mn) is showed in figure 2. As seen in Fig. 2a, the sepiolite had a fibrous morphology with smooth surface and clear boundary grains. The fibers have the length of microns and the width of hundreds of nanometers. After loading manganese oxides, the sepiolite morphology has slightly modified. The surface of the fibers became rougher and the fibrous length is reduced as shown in Fig. 2b.

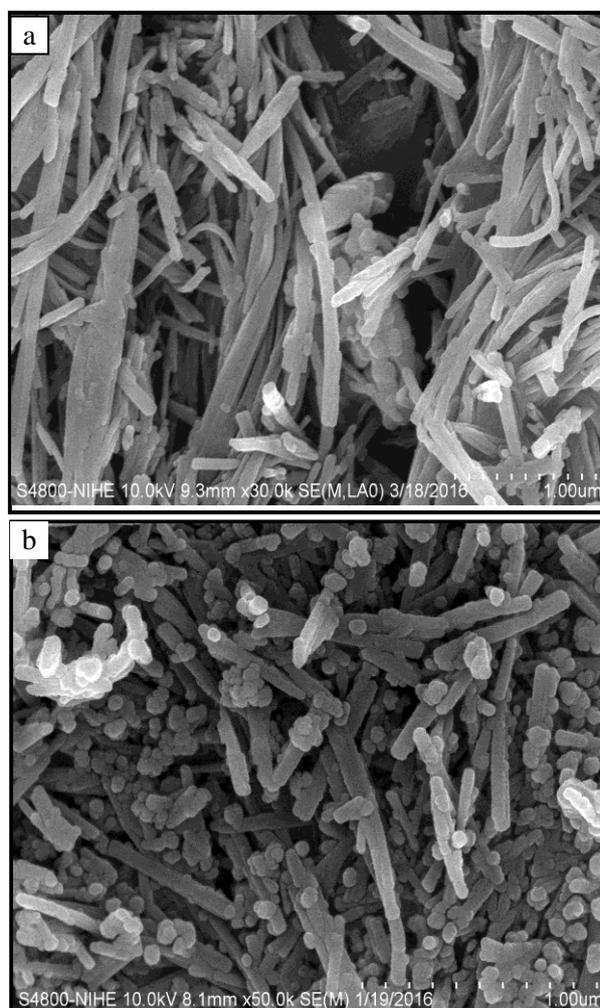


Figure 2: SEM micrographs of sepiolite (a) and TNK04-10Mn (b)

Furthermore, there are existence of numerous uniformly rounded particles with the diameter of 100

nm. Thus, the specific surface of MnO_x /sepiolite is expected lower than that of sepiolite parent. Indeed, the specific surface area of sepiolite was $166.2 \text{ m}^2/\text{g}$, while that of the MnO_x -loaded sample (TNK04-10Mn) was about $133.9 \text{ m}^2/\text{g}$ as measured by N_2 adsorption-desorption method (not shown here). The decrease of specific surface area of in the latter case could be attributed to the incorporation of manganese oxide species [16, 17].

3.1.3. H_2 -TPR analysis

The oxidation-reduction property is usually interpreted from the H_2 temperature – programmed reduction (H_2 -TPR). Figure 3 presents a H_2 -TPR profile for a representative sample of MnO_x /sepiolite recorded from room temperature to $800 \text{ }^\circ\text{C}$. The stages of the reduction has been explained as the phase evolution accompanied with valence development of manganese 8. As shown in Fig. 3, H_2 -TPR profile displays a couple of hydrogen consumption signals. The low temperature reduction peak ($< 200 \text{ }^\circ\text{C}$) corresponds to the oxidation of the absorbed oxygen species on the catalyst surface without decomposition of the material 9. The peak at $410 \text{ }^\circ\text{C}$ is firmly ascribed as the reduction of Mn_3O_4 to MnO , in good accordance with the data reported in the literature 12. It is noted that in some reports, Mn_3O_4 may also be reduced in a two-stage reduction instead of one step because the reduction of MnO_x was also dependent on the different manganese precursors and catalyst preparation method 14.

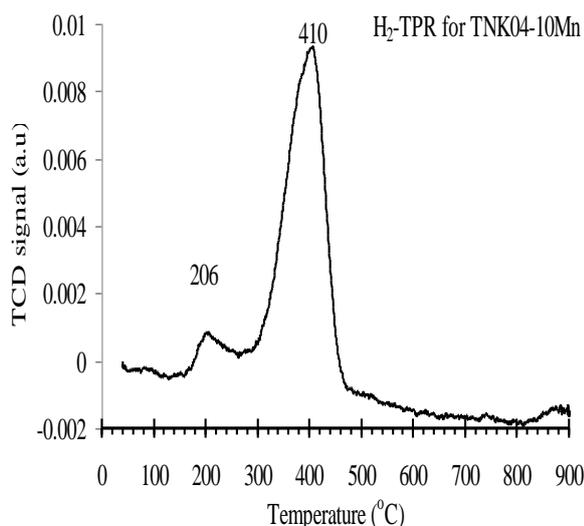


Figure 3: H_2 -TPR profile of TNK04-10Mn sample

Thus, H_2 -TPR analysis reaffirmed the existence of Mn_3O_4 phase in the synthesized MnO_x /sepiolite sample, in good agreement with XRD results shown in Fig. 1.

3.2. Catalytic activity

The oxidation reaction of benzyl alcohol over MnO_x /sepiolite catalysts with *tert*-butyl hydroperoxide solution was performed at atmospheric pressure and the temperature range of $50\text{--}90 \text{ }^\circ\text{C}$. It is well known that the oxidation reactions were strongly dependant on reaction conditions as catalyst dosage, temperature, nature of oxidizing agent, solvent... [19, 20]. In this work, we are interested in the effect of reaction time and temperature on the selectivity of the desired products.

For the sake of comparison, a blank experiment was made using sepiolite calcined at $410 \text{ }^\circ\text{C}$. The conversion of benzyl alcohol was observed only 2 % at $70 \text{ }^\circ\text{C}$ temperature for 4h while TNK04-10Mn exhibited 18 % of benzyl alcohol conversion in the same reaction conditions. These prove that an introduction of MnO_x on sepiolite has promoted the catalytic oxidation of benzyl alcohol to benzaldehyde [9, 15, 18]. Therefore, we continued to carry out in the reaction temperature range of $50\text{--}90 \text{ }^\circ\text{C}$. The results were illustrated in Fig. 4.

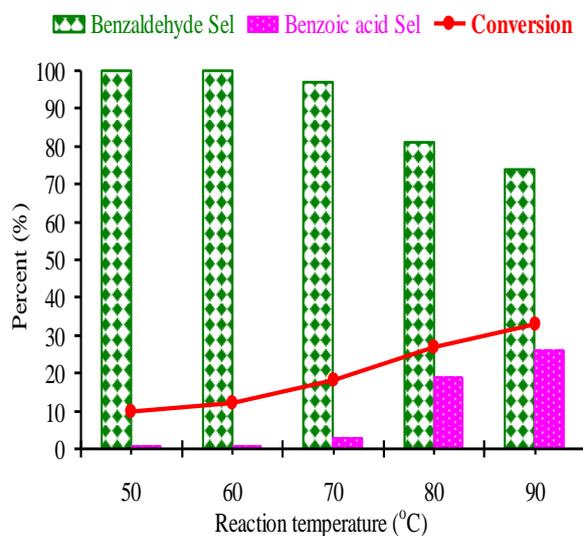


Figure 4: Effect of reaction temperature on catalytic activity of sample TNK04-10Mn (10 wt.% Mn^{2+} /sepiolite) for 4 h, TBHP/BA = 1.5 mol

As being expected, Fig. 4 displays a significant influence of reaction temperature on benzyl alcohol conversion. Although the catalyst likely produced a single product at lower reaction temperature of $50\text{--}60 \text{ }^\circ\text{C}$, but the yield for benzaldehyde is somewhat small due to a moderate conversion of benzyl alcohol obtained at these conditions. An increased reaction temperature gave rise to higher conversion of benzyl alcohol, but there is appearance of small

amounts of benzoic acid as a secondary product. The latter acid was possibly resulted from the over-oxidation of benzaldehyde [4, 19]. Therefore, it is suggested that 70 °C is the most appropriate temperature for the selective oxidation of benzyl alcohol to benzaldehyde product over MnO_x/catalysts in the present work.

Another process to approach a better conversion of benzyl alcohol is to prolong the reaction at a low temperature. Thus, a series of experiments have carried out at 60°C and kept the reaction mixture in a batch reactor for periods of 2-10 h.

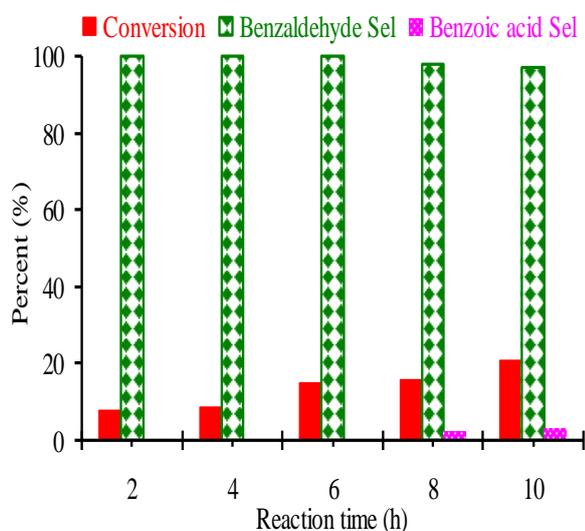


Figure 5: Effect of reaction time on catalytic activity of sample TNK04-5Mn (5 wt.% Mn²⁺/sepiolite) at 60 °C, TBHP/Benzyl alcohol = 1.5 mol, none solvent

Figure 5 presents the catalytic activity for a longer reaction time. It is clearly observed that the an increased both benzyl alcohol conversion and benzaldehyde selectivity with increasing reaction time [5, 9, 19]. Obviously, benzyl alcohol conversion continuously increases linearly from 8 to 22 % while selectivity for benzaldehyde was almost remained constant. There is only small amount of benzoic acid (< 3 %) formed after 8-hour-reaction, reflecting a high selective activity of MnO_x/sepiolite catalysts in the oxidation of benzyl alcohol.

4. CONCLUSION

With XRD pattern of sepiolite and MnO_x/sepiolite analyzed; manganese oxide existed as Mn₃O₄ on sepiolite nanofibers after the precipitation from nitrate salt. The morphology of sepiolite was slightly modified after calcination process. The Mn₃O₄ particles were well distributed on the surface of the fibrous sepiolite and caused slight decrease in

specific surface area of the support. Under hydrogen flowrate, Mn₃O₄ was reduced into MnO in a single step and well dispersed on carrier. The MnO_x/sepiolite catalyst showed a good ability to conversion benzyl alcohol into benzaldehyde. The benzyl alcohol conversion varies from 10-33 % while the benzaldehyde selectivity may approach to 99 % at a given condition. The catalytic activity strongly depends on reaction conditions.

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