Thermal Catalytic Oxidation of Toluene by K-OMS 2 Synthesized via Novel Uncalcined Route

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***Abstract*—**Octahedral molecular sieve type manganese oxide was prepared through a hydrothermal, uncalcined process. Central composite design was used to get the optimum hydrothermal temperature and time setting where toluene decomposition was used as the response. XRD patterns and SEM images obtained show good crystallinity and formation of OMS-2 nanofibers at 90^{o}C and its transformation to OMS-7 nanorods was found to be at 150^{o}C. In addition to this, a decrease in crystallinity was found at longer hydrothermal time and higher temperature.

The OMS-2 obtained gave high percent toluene removal and the optimum hydrothermal setting was found to be 102^{o}C, 3 h. The data obtained were accurate and the r^2 obtained from the predicted vs actual values was 99.35% which implied that the model used has good approximation of the actual data.

***Keywords*—**Hydrothermal, Octahedral Molecular Sieve, Toluene

I. Introduction

Toluene is known to be one of the most common volatile organic compounds (VOCs) in the atmosphere that pollute the quality of air. It is widely produced from domestic activities and industrial processes [1]. Due to its immensity and innumerable sources, it was found to have adverse effects on human health. Because of this, the US Occupational Safety and Health Administration (OSHA, 2004) set 200 ppm for an 8 h workday as a regulatory value for indoor toluene exposure [2].

As a result of the demand to effectively reduce toluene, thermal catalytic oxidation was studied [3]. In the case of VOC oxidation, Octahedral Molecular Sieve (OMS) type manganese oxide is identified as a very active catalyst [4] Its form with one dimensional 2x2 structures known as OMS-2 has mixed-valence, porous structure, excellent hydrophobicity and strong affinity towards VOCs and thus has the highest activity among the OMS group. In addition to this, it is considered low cost and non-toxic [5]. A lot of studies were done to produce OMS-2. However, these methods involve calcination which makes them expensive. As compared to other preparation processes, hydrothermal does not require calcination which favors easier formation of Mn6+ and thus permits facile OMS-2 preparation and makes it relatively inexpensive.

The aim of this research was to synthesize OMS-2 via uncalcined route and to use Central Composite Design (CCD) to investigate the main and interaction effects of hydrothermal temperature and time in the synthesis on the thermal catalytic oxidation of toluene..

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II. Methodology

A. K-OMS 2 Synthesis

$Mn(CH_3COO)_2$ and $KMnO_4$ with 0.75 molar ratio were individually dissolved in 50 mL distilled water. $KMnO_4$ solution was then added to $Mn(CH_3COO)_2$ dropwise and the pH of the mixture was adjusted by glacial CH_3COOH until acidic. It was then put in an autoclave inside an oven under different hydrothermal temperature and time settings. The black slurry obtained was then washed, filtered and dried at 100^{o}C for 4 h and then 200^{o}C for another 3 h.

B. Determination of the Optimum Hydrothermal Setting and Toluene Decomposition

Central Composite Design (CCD) was used to determine the optimum time and temperature settings for K-OMS 2 synthesis. Thirteen samples were obtained based on Table 1. After the samples were obtained, thermal catalytic decomposition of toluene was done. Toluene was maintained at -3^{o}C and was supplied using an evaporation bath. It was then passed through the catalyst for 10 minutes. Percent toluene removal was measured using Gas Chromatography with Thermal Conductivity Detector (GC-TCD). Results were then plotted and compared.

C. K-OMS 2 Characterization

The formation of K-OMS 2 was confirmed using X-ray Diffractometer (Model D8 Discover, Bruker AXS Germany)

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using CuKα with wavelength (λ = 1.51418oA) at 40 mA and 40kV with 2θ range of 10-80 degrees and increasing step of 0.02 degrees. The morphology of the samples were investigated using Scanning Electron Microscope (SEM Model S-3000N Hitachi Japan).

TABLE I
CCD FOR DETERMINING OPTIMUM HYDROTHERMAL CONDITION

Factors (Hydrothermal)	Levels				
	-α	-1	0	1	α
Time	3	6	12	18	21
Temperature	75	90	120	150	165

III. RESULTS AND DISCUSSION

The synthesis of manganese oxide with tunnel structures follows a two-step, dissolution-recrystallization process. Dark brown solution known as birnessite was produced when $KMnO_4$ was added to the $Mn(CH_3COO)_2$ solution. These layered structures were balanced by K+ ions in the interlayers and were then dissolved upon changing the pH. During hydrothermal process, tunnel structures referred to as K OMS-2 were then formed as shown in the XRD patterns in Fig 1 where the main peak of cryptomelane was visible at 2θ = 37.5^o [6] for the catalyst synthesized at 90^{o}C, 6 h. The start of transformation of OMS-2 to the less active OMS-7 was marked by the decrease in the intensity of the peaks at 150^{o}C, 6 h and this transformation was further observed at 150^{o}C, 18 h shown by the very sharp peak of OMS-7 at 2θ approximately equal to 26^o in Fig. 1.

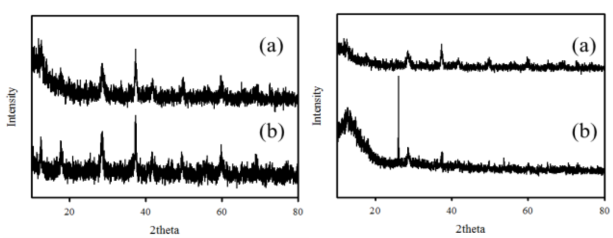

Fig. 1 XRD patterns left: comparison of hydrothermal temp (a) 150^{o}C, 6 h (b) 90^{o}C, 6 h right: comparison of hydrothermal time (a) 150^{o}C, 6 h (b) 150^{o}C, 18 h

The transformation was also observed in the SEM images shown in Fig 2 where the nanofibrous OMS-2 changed into a nanorod like OMS-7. This can be explained by the removal of K^+ supporting the inside of the tunnels which then leads to the collapse of the less crystalline 2 x 2 OMS-2 tunnels and transformation of these to 1 x 1 more thermally stable tunnels called OMS-7.

The main and interaction effects of hydrothermal temperature and time on catalytic activity of the OMS-2 produced are shown in Fig. 3. It can be observed that all the activity only increased at temperature up to 120^{o}C and it already decrease when temperature was set higher than 120^{o}C and when time was increased. However, high increase in hydrothermal temperature showed the higher effect as shown in the slope of the main effects plot. This is due to the phase transformation that happened from 90^{o}C to 150^{o}C which is consistent with the XRD and SEM results. This proved that OMS-2 is more active than OMS-7. In addition to this, all factors were found to be significant at 95% confidence interval except for the high increase in time. On the other hand, the increase in temperature and time partially causes slight mobility of K^+ which also leads to lower crystallinity and lower activity. On the other hand, the curve lines on the contour plot show the interaction of the two factors and give an optimum condition at 102^{o}C, 3 h.

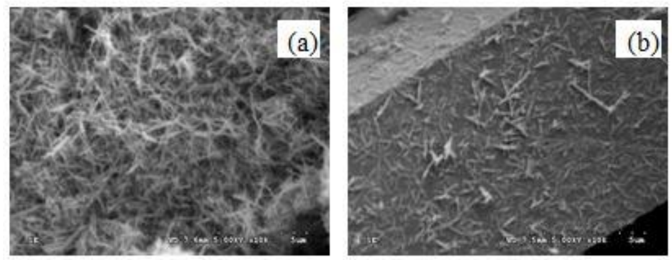

Fig. 2 SEM images of OMS produced at 5000x at (a) 150^{o}C, 6 h (b) 150^{o}C, 18 h

An r^2 of 99.35% was obtained and the lack of fit obtained was insignificant. Thus, the model used for the plots has good approximation of the real data.

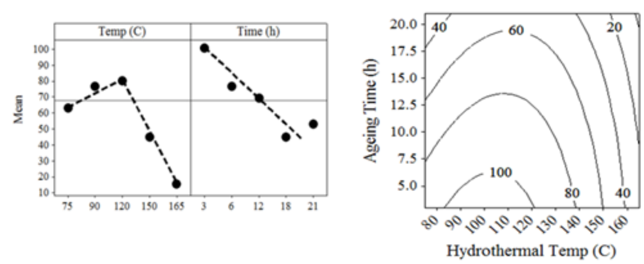

Fig. 3 left: main effects right: interaction effects

IV. CONCLUSION

Hydrothermal method effectively produces OMS-2 even at low temperature. Low hydrothermal temperature and time setting was found to be most favorable in producing OMS-2 because a phase transformation happens at higher temperature and a decrease in crystallinity happens at longer time which may have caused lower catalytic activity of the catalyst.

The data obtained are accurate and hydrothermal temperature and time are significant and have interaction effect on the catalytic activity. In addition to this, toluene was efficiently oxidized having 100% as the highest percent removal.

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