# Abatement of Benzyl Alcohol and Methyl Ethyl Ketone (MEK) from Polluted Air Over Nanostructured Mn -Supported Alumina Catalyst

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**Abstract**

*Total combustion of methyl ethyl ketone and benzyl alcohol as two models of volatile organic compounds (VOCs) using catalytic method was studied over $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ catalysts. Catalyst (Mn/$\gamma$-Al$_2$O$_3$) was prepared by wet impregnation and characterized using XRD, BET, ICP-AES and SEM methods and the nanostructure of the catalyst were approved. The activity of the catalysts was measured in a catalytic packed bed reactor under atmospheric pressure and different reaction temperatures at range 150 to 450°C. The studies confirmed that manganese supported on $\gamma$-Al$_2$O$_3$ can be suitable for the abatement of the mentioned pollutants from contaminated air and hopefully holds the promise for the elimination of VOC containing hazardous materials in industrial applications.*

**Keywords:** *Mn/$\gamma$-Al$_2$O$_3$, VOCs, Catalytic Oxidation, Benzyl Alcohol, Methyl Ethyl Ketone*

## 1- Introduction

Abatement of pollutant volatile organic compounds (VOCs) has become one of the most important tasks for air pollution control. Among the VOCs, methyl ethyl ketone (MEK, 2-butanone) and benzyl alcohol are two of the main pollutants [1]. Methyl ethyl ketone is a ketone widely used as solvent in many industrial applications such as adhesives and paints. In addition, it is a natural component in food stuffs [2]. It is released into the environment from such sources as building materials, consumer products, and tobacco smoke [3]. It is hazardous and its emission into the atmosphere has to be controlled according to environmental regulations [4]. From the human health viewpoint, this odorant can be harmful even below its normal human perception level. The odor threshold values of this VOC have been prescribed by various authors and agencies such as 5400 ppb, by The United States Environmental Protection Agency (EPA) [5], and 440 ppb prescribed by Nagata and coworkers [6]. Benzyl alcohol, an aromatic primary alcohol, is used as a solvent in paint stripper and waterborne coating applications and as an intermediate

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for the synthesis of target molecules used in pharmaceuticals, cosmetics, preservatives, and flavoring and fragrance agents [7]. This alcohol is one of the pollutant VOCs and its abatement is necessary [8].

The oxidation of the VOCs is a way for removing these pollutants from the environment. The oxidation on catalysts takes place at temperatures which are lower than those required for thermal destruction [9]. This is important in order to improve the economy of the process. In the catalytic incineration, VOCs react with oxygen (usually, most of the VOCs emissions are diluted in air) in the presence of a catalyst, yielding $H_2O$ and $CO_2$ without the formation of by-products and in such processes, partial oxidation reactions must be avoided. According to much stricter limits for the emissions of some oxidized compounds, the presence of even small amounts of species like aldehydes, can make the mixture resulting from catalytic combustion processes even more of a pollutant than the waste to be purified [10-16].

Nanostructure catalysts are of topical interest because of their intriguing properties different from those of their corresponding bulk catalysts. Due to their unique properties, they were employed in various catalytic applications. There are many reports in the literature on the synthesis of transition metal nanoparticles and their application as catalysts [17-20]. The metal oxide particles are the key compounds of the catalyst. They are responsible for the activity and selectivity of the catalyst. The activity of the catalyst will generally depend on the size of the metal oxide particles, where a catalyst with small particles will give high activity due to the

large number of atoms available on the particles surfaces [21].

## 2- Material and methods
### 2.1- Materials
The commercial nanostructure $\gamma$-$Al_2O_3$ powder (BET=190 $m^2$/g) was supplied by Merck industry and was used as a catalyst without further purification or treatment. The precursor metal salt, $Mn(NO_3)_2$ was also purchased from Merck Industry. All the other solvents and chemicals were obtained from commercial sources and were used without further purifications.

### 2.2- Preparation of Mn/$\gamma$-$Al_2O_3$ nano particles
Wet impregnation method was used for loading the metal on the support surface. The $\gamma$-$Al_2O_3$ particles was added to 0.1 M aqueous solution of $Mn(NO_3)_2$ and stirring was carried out for 12 h at room temperature. Afterward, the resulting emulsion was centrifuged and filtered using deionized water several times. Mn/$\gamma$-$Al_2O_3$ catalyst was obtained after drying at 105°C and consequently calcinating in air at 450°C for 4h. The prepared Mn/ $\gamma$-$Al_2O_3$ contains 4.6 wt. % of manganese and its surface area was 145.5 $m^2$/g.

### 2.3- Characterization of catalysts
The $\gamma$-$Al_2O_3$ and Mn/$\gamma$-$Al_2O_3$ were characterized by XRD, SEM, BET and ICP-AES methods. Powder X-ray diffraction (XRD) was used to identify the crystalline phase presence in the catalysts. A Siemens D500 diffractometer with Cu $K_\alpha$ ($\lambda$=0.154 nm) radiation was used. The morphology study of the catalysts was studied using scanning electron microscopy (SEM). The

images of the samples were recorded on a EQ-C1-1 microscope. Brunauer-Emmett-Teller (BET) surface areas of the samples were determined by $N_2$ adsorption-desorption using a Micrometrics (Gimini2375) surface area analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method was used for determining the amount of metal loaded on the support (based on the weight percent of metal in the final catalyst).

**2.4- Determination of catalyst activity**

The activity of the catalysts was measured in a 0.8 cm i.d continuous flow tubular glass reactor fixed in an experimental set up shown in Fig. 1. Catalyst (0.2 g) was placed over a plug of glass wool and placed inside of a U shaped reactor. The $N_2$ flow is used as the carrier gas for evaporation of VOC (MEK and benzyl alcohol) and purified air is used as the oxygen supplier flow. The feed gases were pre-mixed in the mixing chamber and sent to the reactor. The reaction was operated under steady state in atmospheric pressure. Gas phase products of the reaction were trapped and analyzed by gas chromatography using Shimadzu 2010 GC. The fractional conversion of VOC ($X_{VOC}$) in this study is defined as equation (1).

$$X_{VOC} = \frac{N_{initial} - N_{final}}{N_{initial}} \tag{1}$$

Where $N_{initial}$ is moles of VOC present initially and $N_{final}$ is moles of VOC present after the reaction completes.
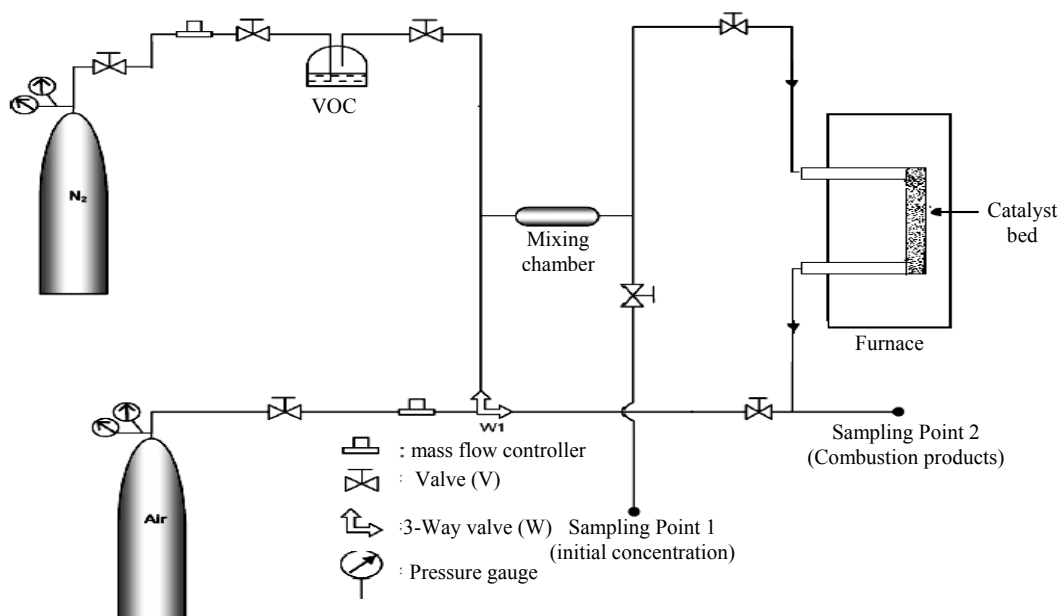


**Figure 1.** Schematic of experimental setup

# 3- Results and discussion

## 3.1- XRD characterization of catalysts

Fig. 2 shows the XRD patterns of $\gamma$-$Al_2O_3$ and Mn/$\gamma$-$Al_2O_3$ samples. Three intense characteristic peaks of $\gamma$-$Al_2O_3$ ($2\theta$= 37°, 45° and 67°) were observed in both spectra, which was in agreement with the published literature [22, 23]. The crystal size of the $\gamma$-$Al_2O_3$ was determined using Scherer equation through the XRD pattern of $\gamma$-$Al_2O_3$, which was in nano scale (approximately 25-30 nm). From the Mn/$\gamma$-$Al_2O_3$ pattern, typical diffraction peaks of crystalline Mn oxides cannot be observed, except those of $\gamma$-$Al_2O_3$ support. In addition, decreasing the intensity of characteristic peaks corresponding to $\gamma$-$Al_2O_3$ can be observed. It seems to suggest that through the impregnation of $\gamma$-$Al_2O_3$ the adsorption of the salt solution has occurred and during the drying and calcination in air the Mn-oxide particles have been formed and physically supported on the $\gamma$-$Al_2O_3$ surface in high dispersion form. The above conclusion is reasonable if we accept that the Outer-Sphere complex has been formed when the adsorption of $Mn^{2+}$ occurs [24].

## 3.2- Scanning electron microscopy

The scanning electron micrographs of both $\gamma$-$Al_2O_3$ and Mn/ $\gamma$-$Al_2O_3$ catalysts are shown in Fig. 3. The particles of the $\gamma$-$Al_2O_3$ are small (< 100 nm) and they have an approximately similar size. SEM images approved the particle size of $\gamma$-$Al_2O_3$ predicted by Scherer equation. Mn/ $\gamma$-$Al_2O_3$ particles are more agglomerate compared to $\gamma$-$Al_2O_3$.
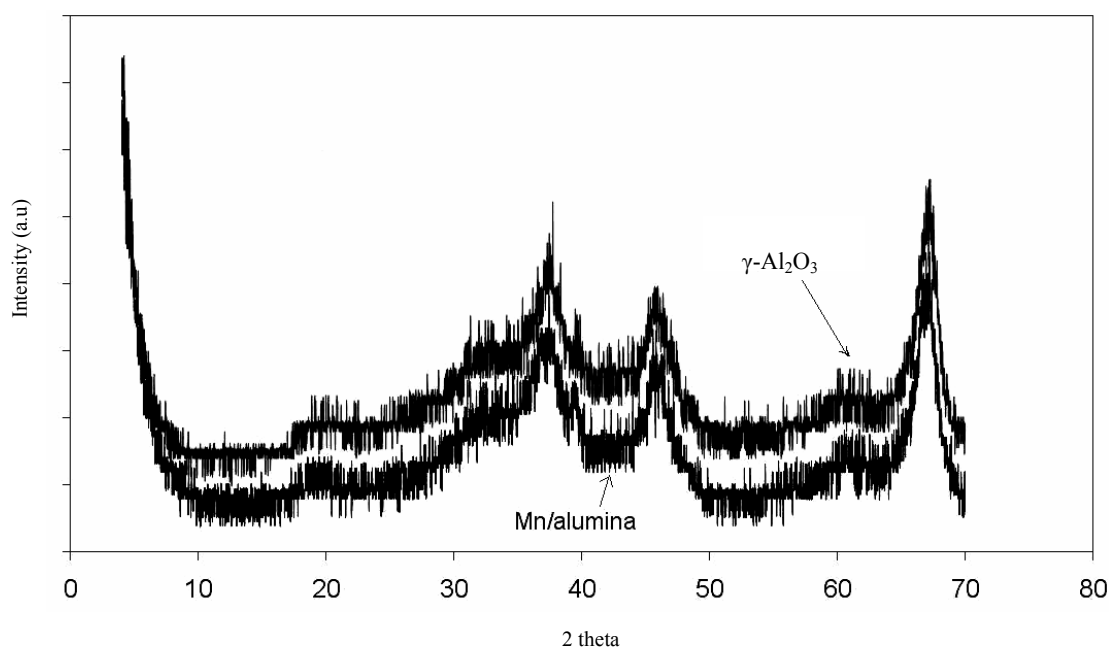


**Figure 2.** XRD pattern of $\gamma$-$Al_2O_3$ and Mn/ $\gamma$-$Al_2O_3$
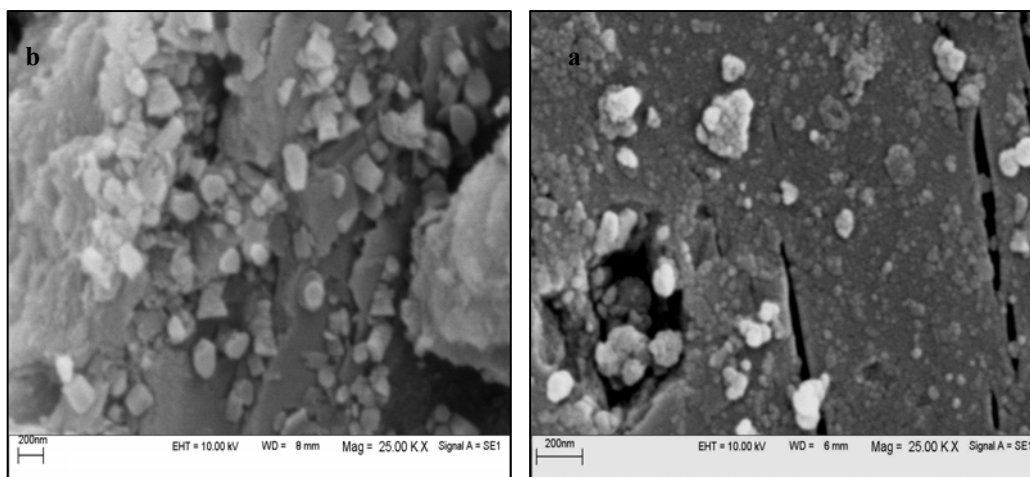
**Figure 3.** SEM patterns of (a) $\gamma$-Al$_2$O$_3$ (b) Mn/ $\gamma$-Al$_2$O$_3$

### 3.3- Catalytic activity

To study the catalytic activity of catalysts for conversion of VOCs, conversions of methyl ethyl ketone and benzyl alcohol over $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ were investigated. At first, the conversion of these compounds in absence of catalyst at different temperatures (thermal oxidation) were studied. Afterwards, $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ catalysts were tested. Light-off curves of conversion of benzyl alcohol in the absence of catalyst (thermal oxidation), and over $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ catalysts are shown in Fig. 4. In the absence of catalyst, a maximum conversion of 27% resulted for benzyl alcohol at 450 °C and at lower temperatures the conversion is very low. Conversion of benzyl alcohol over $\gamma$-Al$_2$O$_3$ is more than the conversion of benzyl alcohol in the absence of catalysts. This shows that at the finite temperature, the efficiency of catalytic oxidation is more than thermal oxidation. In addition, the modification of $\gamma$-Al$_2$O$_3$ with transition metals oxide (here manganese oxide) causes the catalytic

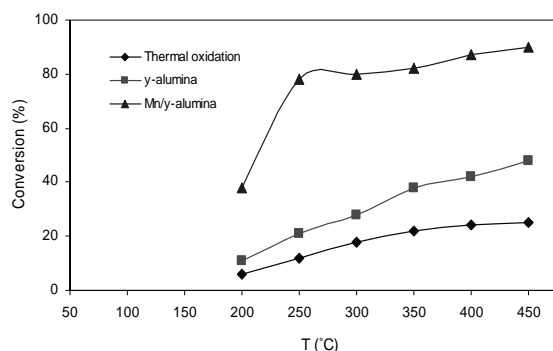activity of catalysts to improve, revealing the catalytic roles of these oxides in the Mn/$\gamma$-Al$_2$O$_3$.



**Figure 4.** Light-off curves of conversion of benzyl alcohol

A similar trend was obtained for the conversion of methyl ethyl ketone (MEK) the and following order resulted for the conversion of MEK: thermal oxidation < $\gamma$-Al$_2$O$_3$ < Mn/$\gamma$-Al$_2$O$_3$. The maximum conversion of MEK at thermal oxidation is 24 % at a temperature of 450 ˚C.

It is observed that the conversions of benzyl

alcohol and MEK differ in the definite temperature. This is because of the difference in the molecular structure of organic compounds and their reactivity on catalysts.
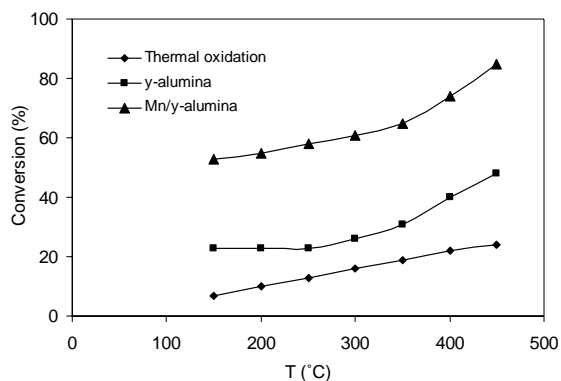


**Figure 5.** Light-off curves of conversion of MEK

## 4- Conclusions

Catalytic conversions of benzyl alcohol and MEK on nanostructure pure and Mn-supported $\gamma$-Al$_2$O$_3$ were studied. The studies show the better efficiency of catalytic oxidation compared to thermal oxidation for the conversion of organic compounds. In addition, it is resulted that the introduction of manganese onto $\gamma$-Al$_2$O$_3$ improves the activity of Mn/$\gamma$-Al$_2$O$_3$, which confirms the catalytic role of manganese in Mn/$\gamma$-Al$_2$O$_3$. It is concluded that Mn/$\gamma$-Al$_2$O$_3$ catalysts can be used as suitable catalysts in the catalytic conversion of organic compounds.

## 5- Acknowledgement

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