Investigation of the Activity of Nano Structure Mn/γ-Al_2O_3 Catalyst for Combustion of 2-Propanol

D. Salari, A. Niaei*, S. A. Hosseini, R. Aleshzadeh, H. Afshary

Department of Chemical Engineering and Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, I. R. Iran

(*) Corresponding author: niaei@yahoo.com
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Abstract:

This paper reports results of a study regarding the activities of nano structure Mn/γ-Al_2O_3 and γ-Al_2O_3 catalysts for oxidation of 2-propanol (as a model of volatile organic compound). Nanostructure of catalysts was revealed using XRD, SEM and TEM techniques. Catalytic studies were carried out in U-shaped packed bed reactor under atmospheric pressure and at the reaction temperature of 150- 500°C. Results showed that the introducing of manganese onto γ-Al_2O_3 improves the activity of Mn/γ-Al_2O_3 compared to pure γ-Al_2O_3 for oxidation of 2-propanol. This study confirms that nanostructure Mn/γ-Al_2O_3 catalysts can be suitable for oxidation of organic compounds. This study, hopefully, holds the promise for the eliminating of 2-propanol contained hazardous materials in industrial application.

Keywords: *Nano structure γ-Al_2O_3, Mn/γ-Al_2O_3, Isopropanol, VOC, Catalytic oxidation*

1. INTRODUCTION

Air pollution has become one of the most complex environmental problems. Among the most common sources produced by volatile organic compounds (VOCs), 2-propanol is one of the main pollutants whose principal sources are cleaning fluids and vehicles (2-propanol is a major ingredient in "dry-gas" fuel additives). It is about twice as toxic as ethanol and its metabolite, acetone, is a CNS depressant in its own right. It was the fifth on the list of 12 most commonly poisoning drugs in a study undertaken in the USA [1].

The oxidation of the VOCs to CO_2 and H_2O is a promising method for removing these pollutants from environment. The oxidation on catalysts takes place at temperatures, which are lower than those required for thermal destruction which is an important factor for improving the economy of the process [2]. In the catalytic incineration, VOCs react with oxygen (usually the most VOC emissions are diluted in air) in 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 more strict restriction 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 pollutant than the waste to be purified [3].

There are two types of catalysts that can be used in catalytic oxidation, i.e. metal oxides and supported noble metals [4-7]. It is generally accepted that noble metals are more active than metal oxides but the latter are more resistant to poisoning [8]. Pt and Pd are the most common noble metals used for total oxidation of VOCs [9] but their high costs

and limited availability have been encouraging their replacement by other active compounds such as metal oxide/Al_2O_3 catalysts.

Nano structure 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 applications as catalysts [10-13].

Alumina has enormous technological and industrial applications. It exists in a variety of metastable structures including γ, η, δ, θ, κ and χ-alumina, as well as its stable α-alumina phase [14]. Among these transitions, γ-alumina is one kind of extremely important nano sized materials. It has been used as a catalyst and catalyst substrate in automotive and petroleum industries, structural composites for spacecraft, and abrasive and thermal wear coatings [15]. Recently Al_2O_3 in pure and support forms has been widely used for eliminating many organic pollutants [16-18]. Complete oxidation of BTX (benzene, toluene, xylene) over some metal oxides (Cu, Mn; Fe, V, Mo, Co, Ni, Zn) supported on γ-Al_2O_3 and other supports was reported by Kim et al. [19]. Results of their study showed that γ-Al_2O_3 was most promising support from the view point of activity.

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 [20].

In the present work we studied the activity of γ-Al_2O_3 and Mn/γ-Al_2O_3 catalysts (both in nano size) for deep oxidation of Isopropyl alcohol. The aim of this work was to determine the effect of γ-Al_2O_3 particle size and the presence of metal oxide (Mn oxide) on the activity of catalyst in the oxidation of 2-propanol.

2. MATERIAL AND METHODS

2.1. Materials

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

2.2. Characterization methods

The catalytic materials 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 Kα (λ=0.154 nm) radiation was used. The morphology study of catalysts was studied using scanning electron microscopy (SEM). The image of samples was recorded on EQ-C1-1 microscope. The Brunaure-Emmet-Teller (BET) surface areas of the samples were determined by N_2 adsorption-desorption using a Micrometrics (Gemini2375) surface area analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method was used for determining the amount of metal loaded on support (based on weight percent of metal in final catalyst). TEM measurements were carried out in a JEOL 2000 electron microscope operating at 200 kV.

2.3. Preparation of Mn/γ-Al_2O_3 nano particles

Wet impregnation method was used for loading of metal on support surface. The γ-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 the room temperature. Afterward resulting emulsion was centrifuged and filtered using deionized water for several times. Mn/γ-Al_2O_3 catalyst was obtained after drying at 105°C and consequently calcinations in air at 450°C for 4h. The prepared Mn/ γ-Al_2O_3contains 4.6 wt.% of manganese and it's surface area was 145.5 m^2/g.

2.4. Determination of catalyst activity

The activities of catalysts were measured in a 0.8 cm internal diameter continuous flow tubular glass reactor placed in an electrical furnace. The schematic of experimental set up is shown in Figure 1. Catalyst (0.2 g) was placed over a plug of glass wool and placed inside of U shaped reactor. The N_2 flow is used as the carrier gas for evaporation of VOC (2-propanol) and the purified air 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 the atmospheric pressure. Gas phase products of reaction were trapped and analyzed by a gas chromatography (Shimadzu 2010). The fractional conversion of isopropanol (X isopropanol) in this study is defined as equation (1).

$$X_{isopropanol} = \frac{N_{initial} - N_{final}}{N_{initial}} \quad (1)$$

Where N initial is moles of isopropanol present initially and N final is moles of isopropanol present after the reaction completes.

3. RESULTS AND DISCUSSION

3.1. XRD characterization of catalysts

Figure 2 shows XRD patterns of γ-Al_2O_3 and Mn/γ-Al_2O_3 samples. The characteristic peaks of γ-Al_2O_3 (2θ= 37°, 45° and 67°) was observed in both spectra that was in agreement with published literatures [21, 22]. The crystal size of γ-Al_2O_3 was determined

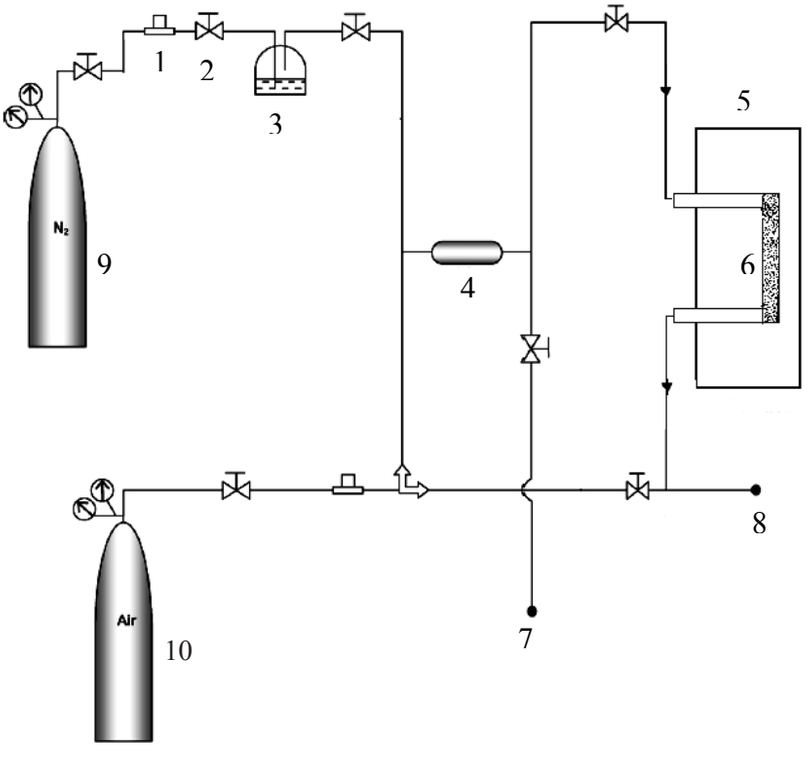

Figure 1: *Schematic of experimental setup*
Mass flow meter (1), Valve (2), VOC saturator (3), mixing chamber (4), electrical furnace (5), U-shaped reactor (6), sampling initial concentration (7), sampling combustion concentration (8), N_2 cylinder (9), air cylinder (10)

using Scherer equation through XRD pattern of γ-Al_2O_3, which was in nano scale (approximately 25-30 nm). From the Mn/γ-Al_2O_3 pattern, typical diffraction peaks of crystalline Mn oxides cannot be observed except those of γ-Al_2O_3 support. In addition, decreasing the intensity of characteristic peaks corresponding to γ-Al_2O_3 can be observed. It seems to suggest that through the impregnation of γ-Al_2O_3 the adsorption of salt solution has been occurred and during the drying and calcination in air the Mn-oxide particles has been formed and physically supported on γ-Al_2O_3 surface in the high dispersion form. The above conclusion will be reasonable if we accept that the Outer-Sphere complex has been formed when the adsorption of Mn^{2+} is occurred [23].

3.2. Scanning electron microscopy

The scanning electron micrographs of both γ-Al_2O_3 and Mn/ γ-Al_2O_3 catalysts are shown in Figure 3. The particles of the γ-Al_2O_3 are small (<100 nm) and they have approximately similar size. SEM images approved the nano structure of γ-Al_2O_3 predicted by Scherer equation. The morphology of Mn/γ-Al_2O_3 is present in Figure 3.b. There are more small particles in SEM micrograph of Mn/γ-Al_2O_3 compared to γ-Al_2O_3, which is ascribed to the presence of manganese oxides.

3.3. Transmission electron microscopy

To confirm the nano structure of catalysts, TEM images were taken. The TEM images of catalysts are present in Figure 4. Because of agglomeration of particles (Figure 4.a), detection of discrete particles is difficult, but it can be observed some particles with size less than 100 nm. Figure 4.b shows the TEM image of Mn/γ-Al_2O_3. The black spots in these images are ascribed to manganese oxides. These images approve the results predicted by Scherer formula and obtained by SEM.

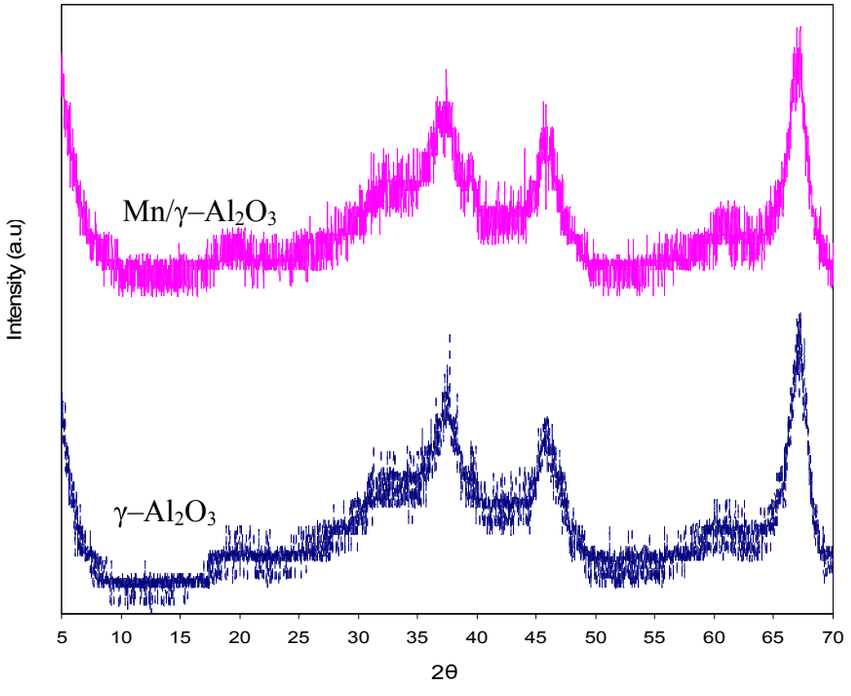

Figure 2: *XRD pattern of γ-Al_2O_3 and Mn/γ-Al_2O_3*

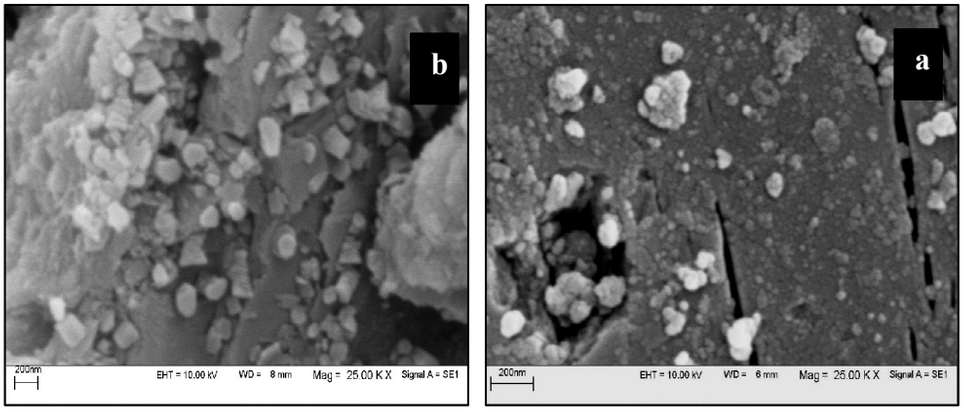

Figure 3: *SEM pattern of (a) γ-Al_2O_3 (b) Mn/γ-Al_2O_3*

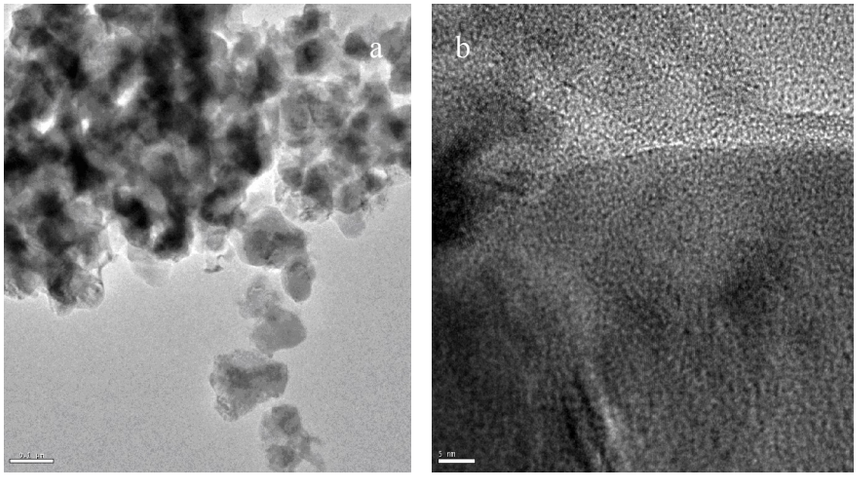

Figure 4: *TEM images of (a): γ-Al_2O_3 (scale: 0.1 μm) and (b):Mn/γ-Al_2O_3*

3.4. Catalytic activity

To study the catalytic activity of catalysts, conversions of 2-propanol over γ-Al_2O_3 and Mn/γ-Al_2O_3 were investigated. At First we studied the conversion of 2-propanol at absence of catalyst at different temperatures (thermal oxidation). Light-off curve for this study is shown in Figure 5. At the absence of catalyst maximum conversion of 30% was resulted for 2-propanol at 450°C and at lower temperatures the conversion is very low. Since all sampling are carried out after establishing steady state condition and 30 min after each run, we sure that the conversion is due to oxidation nor adsorption.

Figure 6 shows the light-off curves of 2-propanol over nano structure pure γ-Al_2O_3 and Mn loaded γ-Al_2O_3. The results show that the conversion of 2-propanol over Mn/γ-Al_2O_3 is higher than that of it over pure γ-Al_2O_3. These results confirmed the higher catalytic activity of Mn/γ-Al_2O_3 respect to pure γ-Al_2O_3. This is attributed to active sites of manganese oxides on the alumina. Since the oxygen atom in 2-propanol has an unpaired electron, it could easily interact with the vacant p-orbital of manganese ion in Mn/γ-Al_2O_3 catalyst leading to the breakage of the C-O bond in the molecule. The interaction of sorbate molecules (2-propanol) with sorbent (Mn/γ-Al_2O_3) could be in the form

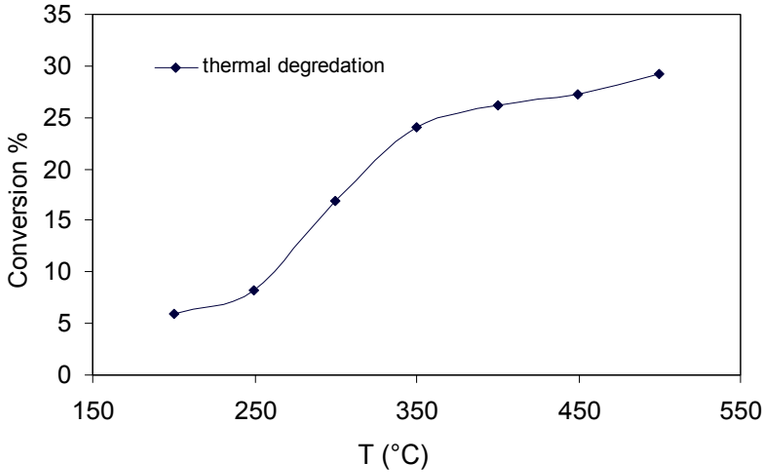

Figure 5: *Light-off curve for thermal oxidation of 2-propanol*

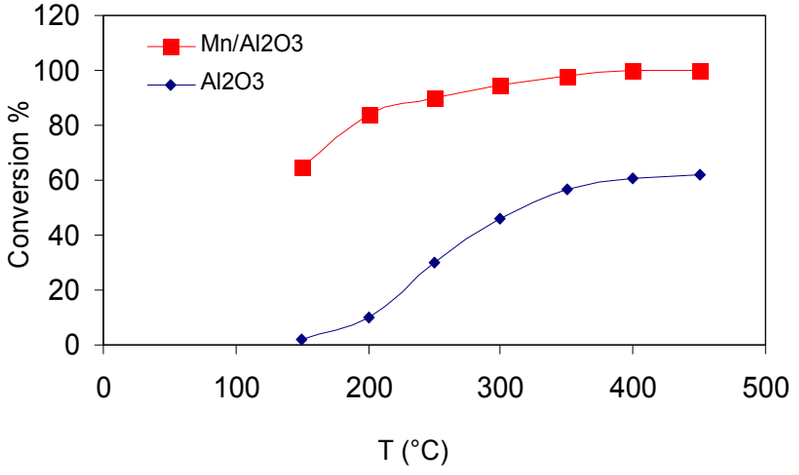

Figure 6: *Light-off curves of 2-propanol oxidation over γ-Al_2O_3 and Mn/γ-Al_2O_3*

of van der Waals forces and electrostatic forces. The magnitude of the forces depends on the polar nature of the sorbate and the sorbent. On polar surfaces, electrostatic forces dominated over van der Waals forces and thus the interaction intensity gets higher.

4. CONCLUSIONS

Catalytic conversion of 2-propanol on nano structure pure and Mn loaded γ-Al_2O_3 was studied. This study shows the better efficiency of catalytic oxidation compared to thermal oxidation for conversion of organic compounds. In addition, it is concluded that introducing of manganese onto γ-Al_2O_3 improves activity of Mn/ γ-Al_2O_3 which confirms catalytic role of manganes in Mn/ γ-Al_2O_3. It is concluded that Mn/ γ-Al_2O_3 catalysts can be used as promising catalysts for catalytic conversion of organic compounds.

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