

Selective Oxidation of Limonene over γ -Al₂O₃ Supported Metal Catalyst with H₂O₂

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ABSTRACT

Liquid phase oxidation of limonene by hydrogen peroxide over the CeO₂ and Fe₂O₃ catalysts supported by γ -Al₂O₃ was reported. Ethyl acetate and acetone were used as solvent to investigate the effect of the solvent on the oxidation reaction. The experiments were carried out at 80 °C. The conversion of limonene and the selectivities of the carvone were calculated during the 10h reaction time. According to experimental results, maximum conversion of limonene and product selectivity of carvone were obtained with CeO₂- γ -Al₂O₃ catalyst as 85% and 41%, respectively end of the 10 h reaction. The XRD analysis of the CeO₂- γ -Al₂O₃ catalyst were performed.

Keywords-- limonene oxidation, carvone selectivity, CeO₂- γ -Al₂O₃ and Fe₂O₃- γ -Al₂O₃ catalyst

from the main reaction formation of 1,2-epoxylimonene-secondary reactions can also occur in this process and formation of the following by-products are observed: 1,2-epoxylimonene diol, 8,9-epoxylimonene, 8,9-epoxylimonene diol, carvone, carveol, diepoxide (1,2 and 8,9), the diol of this epoxide, perillal, perillyl acid and perillyl alcohol [1] [9] [10] [11].

Liquid phase oxidation can be performed with different oxidants and, in the presence of a suitable catalyst, it can take place under relatively mild conditions of temperature and pressure. [9]. Usually, soluble and heterogeneous derivatives of transition metals are used as oxidation catalysts. However, the most efficient catalyst based on transition metals are often expensive. It should be noted, that recently described oxidation reactions with hydrogen peroxide promoted by oxides of non-transition metals aluminium, gallium, or calcium constitute a promising route to various epoxides [2]. Schiff base complexes in particular Metal complexes are often described as good oxidation catalysts, due to their high activities and selectivities [3].

Lima et al. studied limonene oxidation over metal (salen) complexes by using commonly known organic solvents (ethyl acetate, acetone, dichloromethane and acetonitrile) and reactions were carried out 4 h and 24 h. The obtained highest conversion was 94.4 % at room temperature in 24h with ethyl acetate. They have reported that ethyl acetate as solvent showed the best results in terms of conversion and selectivity for both oxidation and allylic oxidation [6]. Wroblewska A. et al, studied limonene oxidation process with Fe/nanoporous carbon catalyst and they reported that the conversion of limonene reached over the 60%. They proposed a method for limonene oxidation and it can be designed as green method [12]. Bonon J. A. et al reported that, aluminium oxide catalysts are highly effective catalysts for the oxidation of olefins with hydrogen peroxides [2]. Prada et al. reported the oxidation of limonene with molecular oxygen using zeolite-Y exchanged with Fe⁺², Co⁺², Mn⁺² and Mo⁺². The best results were obtained with NaCoMoY zeolite, with 53% selectivity to 1,2

I. INTRODUCTION

Limonene is one of the most important intermediate for the production of fine chemicals. It is easy obtained and renewable cheap compound. This monoterpene compound can be obtained from peels of oranges or lemon (biomass) which are wastes produced by the orange juice industry. It has been used in the production of cosmetics, secondary refrigerant fluids, paints, agrochemicals and in the cleaning industries [1] [2]. The oxygenated derivatives of limonene, such as 1,2-epoxylimonene, 1,2-epoxylimonene diol, carvone, carveol and perillyl alcohol are very valuable intermediates used in the production of flavours, perfumes, cosmetics, food additives, drugs, agrochemicals and polymers [3].

The selective oxidation of terpenes is an important process for producing fine chemicals. Oxidation of limonene has been studied by many researchers. The current literature describes limonene oxidation performed by homogeneous [4] [5] [6] and heterogeneous [4] [7] [2] catalytic systems [8]. The studies in the literature revealed that the limonene oxidation process is very complicated because apart

epoxy limonene (57% conversion) [13]. Egusquiza et al. carried out a study of limonene oxidation with H_2O_2 catalyzed by Cu(II) complex heteropoly tungstates and they showed that catalysts with $M(II)=Mn, Co, Cu$ and Zn , good catalytic activity in the oxidation to limonene using H_2O_2 under biphasic conditions [14]. Casascelli et al. carried out a study about the catalytic behavior of molybdophosphoric acid (MPA) or tungstophosphoric acid (TPA), supported on alumina and the lacunar phase of TPA supported on carbon in limonene oxidation with hydrogen peroxide at 70 °C and they found that 59 % selectivity to epoxide [15].

Mlodzik et al. (2016) study that the catalysts in the form of an activated carbon EuroPh supported Fe were prepared and characterized. The catalytic activity of the obtained catalysts was examined in limonene oxidation with hydrogen peroxide and *tert*-butyl hydroperoxide as oxidants. The oxidation of limonene was carried out at the temperature of 70 °C and in the range of the reaction time from 0.5 h to 48 h. According to their results, for the catalysts with the lowest Fe content independent of the used oxidant, formation of carvone was observed [16].

In this study, oxidation of limonene in the liquid phase over $CeO_2-\gamma Al_2O_3$ and $Fe_2O_3-\gamma Al_2O_3$ heterogeneous catalyst has been studied. The metal oxide catalysts were prepared by wet impregnation method. Hydrogen peroxide has been used as clean oxidant. The effect of the solvent selection on the limonene oxidation and catalysts performance were investigated.

II. MATERIALS AND METHOD

Metal salts used to catalyst preparation, $FeSO_4 \cdot 7H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$, and hydrogen peroxide (30 wt % aqueous) were purchased from Sigma-Aldrich. Used solvents Ethylacetate (99.5%) and Acetone (99.8%) were obtained from Merck. The commercial lemon oil which is obtained from a local firm is used as the D- limonene (97.5%).

2.1 Catalyst Preparation

The catalysts used in the experiments were prepared with $\gamma-Al_2O_3$ support by the wet impregnation method. The salt of the metals was dissolved in the

distilled water at room temperature. Then, $\gamma-Al_2O_3$ placed in this solution and mixed for 1 h at 80°C and the obtained solution was sonicated in an ultrasonic bath for 1 h. After that, excess of water was evaporated at 100°C in oven for 12 h. Finally, prepared catalysts were calcined at 550°C in tubular oven for 2 hours. In this experimental series the prepared catalysts includes 3.8-3.9 wt% of the metal.

The crystallinity of the best catalyst was characterized with X-Ray diffraction (XRD). The XRD analyses of the catalysts was performed using a Phillips X' Pert Pro multipurpose X-Ray diffractometer operating with a $Cu K\alpha$ radiation over 2θ range of 5-70° and a position sensitive detector with 0.033 step size.

2.2 Oxidation of Limonene

Limonene oxidation reactions were carried out at 80 °C, with $CeO_2-\gamma Al_2O_3$ and $Fe_2O_3-\gamma Al_2O_3$ catalysts by using ethyl acetate and acetone as solvent, in a three necked flask equipped with a reflux condenser and a thermocouple connected to a temperature controller. A measured amount of limonene and solvent at 1/1 mole ratio were added into the flask. The reaction mixture was magnetically stirred and heated. When the reaction mixture attained to desired temperature, certain amount of H_2O_2 and weighted amount of catalyst were added to the reaction mixture, and the reaction was started. The reactions were carried out for 10 hours. During the reaction every 1hour samples were taken from the reaction mixture and analyzed. All samples were analyzed by GC (Agilent 5850) equipped with flame ionization detector. Products were quantified using standard solutions.

III. RESULT AND DISCUSSION

The conversion of the limonene in oxidation reaction and the selectivity of the carvone at 80 °C temperature by using both solvents and catalysts are shown in the Table1.

Table 1. Conversion and selectivity of carvone after 10 h experiments

Solvent	Catalyst	Conversion (%)	Selectivity of the Carvone (%)
Acetone	$Fe_2O_3-\gamma Al_2O_3$	72	35
Acetone	$CeO_2-\gamma Al_2O_3$	81	41
Ethyl acetate	$Fe_2O_3-\gamma Al_2O_3$	74	22
Ethyl acetate	$CeO_2-\gamma Al_2O_3$	85	35

It can be seen from the Table1, maximum conversion of limonene and corresponding limonene oxide selectivity were found 85% and 33.7% at 70 °C using $CeO_2-\gamma Al_2O_3$ catalyst and ethyl acetate solvent, respectively.

3.1 Effect of the Solvent

The nature of solvents was known to have a major influence on reaction kinetics and product conversion in the oxidation of limonene. The used solvent may increase the catalyst performance. Therefore, in this study the effects of solvents on the reaction are investigated as well. Ethyl acetate and

acetone are most commonly used solvents and they are easy obtained, cheap and described as environmentally favorable [17]. The effect of the solvent and catalyst type on the conversion and selectivity during experiments can be seen in Figure 1 and Figure 2, respectively. From the results, using ethyl acetate as the solvents indicated the best catalytic performance and selectivity to carvone after 10h experiments. Even though, acetone is more

polar than ethyl acetate and has the high dielectric constant, ethyl acetate may dissolve the hydrogen peroxide and limonene and it may be easily adsorbed on the catalyst surface to increase the conversion. A.J. Bonon et al. studied the limonene epoxidation reaction kinetic over Al_2O_3 catalyst by using the ethyl acetate as solvent. In their study the conversion of the limonene was obtained over 90 % at 80°C [2].

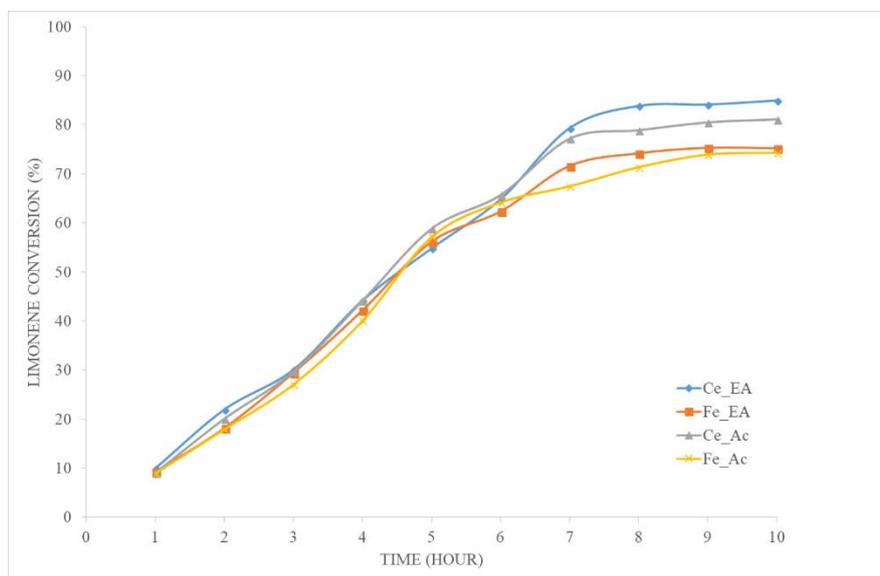


Figure 1. Conversion of the limonene during the oxidation reaction at 80 °C for $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-}\gamma\text{Al}_2\text{O}_3$ catalysts. (EA: Ethyl acetate; Ac: Acetone)

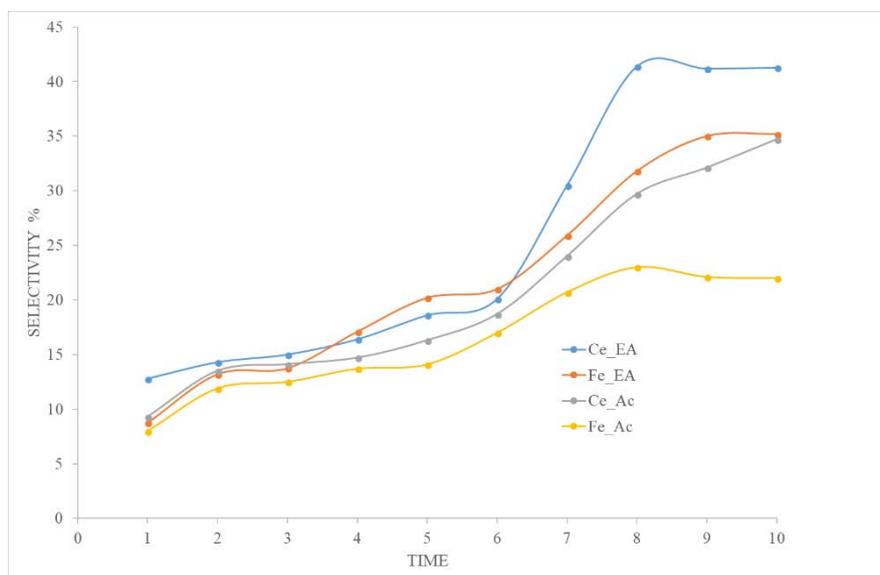


Figure 2. Selectivity of carvone during the limonene oxidation reaction at 80 °C for $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-}\gamma\text{Al}_2\text{O}_3$ catalysts. (EA: Ethyl acetate; Ac: Acetone).

3.2 Effect of the Catalyst

The catalytic activities of $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-}\gamma\text{Al}_2\text{O}_3$ catalysts for limonene oxidation were tested. Both catalysts gave significant conversions and selectivity's. The both conversions and selectivity's were increased with reaction time. After nearly 7 h experiments, the increase of the conversion was very

low. It is apparent from the results that $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ catalyst showed higher conversion and selectivity for carvone.

Maximum limonene conversion and selectivity were obtained over $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ catalyst by using ethyl acetate as solvent at 80 °C.

The XRD patterns of the $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ catalyst are given in Figure 3. The Figure, shows the presence of CeO_2 phase, which the crystal system was found as anorthic. The peaks at 2θ of 37, 50 and 55 are indicates

the CeO_2 crystal formations. The reflections at 2θ of 43, 44 and 67 deals with $\gamma\text{Al}_2\text{O}_3$.

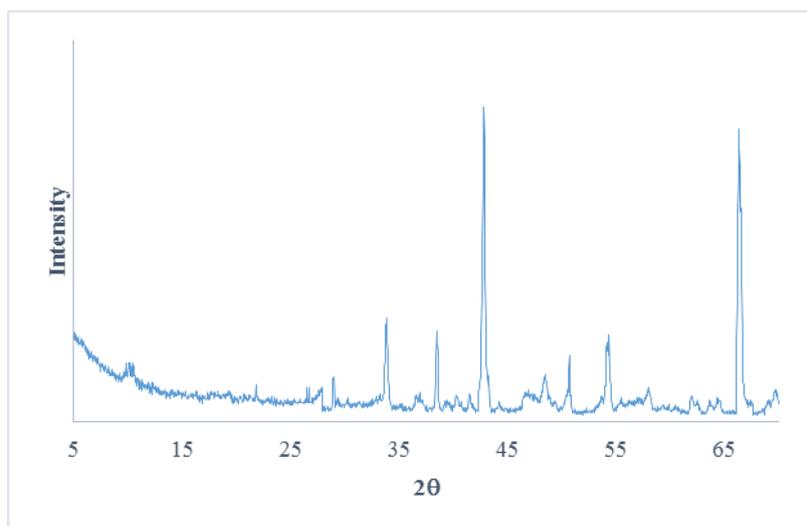


Figure 3. XRD results of the $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ catalyst

IV. CONCLUSION

Limonene oxidation reaction was investigated by using $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-}\gamma\text{Al}_2\text{O}_3$ catalysts. The catalysts were prepared by a wet impregnation method. Hydrogen peroxide has been used as clean oxidant. The effects of reaction parameters of solvent type and catalyst type on the limonene oxidation reaction and carveone selectivity were investigated.

The conversions increased with increasing reaction time as expected. The higher conversions were obtained after 10 h experiments.

Using ethyl acetate as the solvents indicated the best catalytic performance and selectivity towards carveone.

Both $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-}\gamma\text{Al}_2\text{O}_3$ catalysts exhibits considerably significant conversions and selectivity's for carveone.

Oxidation of limonene in the liquid phase can be effectively achieved using $\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ catalyst.

ACKNOWLEDGMENTS

This work was supported by Ege University Scientific Research Projects Coordination (15MUH071).

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