CATALYTIC DEGRADATION OF ETHYL ACETATE OVER V_2O_5 SUPPORTED MOLECULAR SIEVES

A. AGRAWAL†, S. CHANDRA SHEKAR‡, R. TOMAR† and S. GUJARATHI‡

† *SOS Chemistry, Jiwaji University, Gwalior-474011, India. Email: anidha267@gmail.com, Mob: 09999564416*
‡ *Defense Research & Development Establishment, Gwalior, India*

Abstract **- Series of V_2O_5 molecular sieves catalysts with varying vanadium content are prepared by impregnation method. The catalyst composition is determined by AAS, SEM, TPR, XRD and BET Surface area techniques. Ethyl acetate decomposition studies are conducted over V/mol sev catalyst with varying vanadium content in presence of air and ozone in a temperature range of 120 to 180°C. The results reveal that in presence of air the oxidation activity is marginal and the principal oxidation product is ethanol. Whereas in presence of ozone, the oxidation activity is increased significantly, and the primary products are only carbon oxides and the trace amount of partial decomposed products (<10%) are observed. In presence of ozone 82% decomposition activity is observed at 160ºC and all the partial decomposed products are rapidly converting into carbon oxides which are ascribed to the synergetic effect of strong oxidizing nature of ozone and the Vanadia catalysts.**

Keywords**— Degradation, Ethyl acetate, Molecular sieves, Vanadia, VOC.**

I. INTRODUCTION

The developing and developed nations are drastically increasing their industrial system in order to achieve superior gross domestic products (GDP) rates in present scenario. The same results in enormous amount of environmental pollution. Volatile organic compounds (VOCs) are one type of toxic pollutant to environment and produced in variety of industries (Carabineiro and Thompson, 2007; Garetto *et al.*, 2008; Yang *et al.*, 2007; Kim, 2002). Among the various techniques used to control the VOC emission, catalytic combustion is the most preferred one (Yang *et al.*, 2007; Dai *et al.*, 2012; Chandra Shekar *et al.*, 2011; Li *et al.*, 2004; Ihm *et al.*, 2004; Van der Vaart *et al.*, 1991; Allen and Blaney, 1985). This approach is preferred to the thermal one due to the lower temperature required and its greater selectivity, which implies a considerable saving of energy. While the thermal oxidation can be carried out in a range of temperatures between 700 and 1000°C, which leads to NOx production from the N_2 present in air (Eguchi and Arai, 1996). And, in catalytic oxidation, the operation temperature decreases to around 250–500°C, therefore NOx production as well as the energy needed to preheat the stream is much lower (Garetto et al., 2008). In this process, high removal efficiency can be achieved at relatively low temperature by employing the ozone assisted catalytic degradation, which resulted in considerable environmental and economic benefits in comparison to the case of the thermal and catalytic incineration (Yang *et al.*, 2007). Among VOCs, ethyl acetate is a common solvent and is present in various gas exhaust streams, battery operated vehicles, concealed battery based chambers, which can cause severe harm to the human health. It can be completely oxidized to CO_2 by Pd, Pt supported catalyst at about 220–320ºC (Santos *et al.*, 2009). Manganese oxides based catalysts have been extensively studied as catalytic materials in the oxidation of many pollutants such as ethanol, acetone, propane, propene, ethyl acetate and CO. However in case of transition metal oxide catalysts, the probability of forming partial oxidation products has been widely reported. Pradier *et al.* (2000) carried out gas phase combustion of ethyl acetate using CeO, Co_2O_3, Mn_2O_3, Cr_2O_3, and CeO-Co_2O_3 as catalyst and 45% of ethyl acetate conversion was reported at 350ºC. The maximum conversion obtained with the CeO catalyst at 350°C was 72% (Pradier *et al.*, 2000). Similarly, Yuan *et al*. (2008) have reported nearly 99% conversion at 245ºC with Mn/Al_2O_3-Ce0.5Zr0.5O_2 (1:2) catalysts. Here, the present study reports ~82% conversion of EA at 160°C by vapor phase oxidation of ethyl acetate with ozone as an oxidant and V_2O_5 / mol sev as catalyst.

II. EXPERIMENTAL PROCEDURE

A. Preparation and properties of the catalysts

Molecular sieves supported vanadia catalysts of different compositions were prepared by wet impregnation method. For 2 wt% of vanadia catalyst, 1.81 g of Vanadium pentoxide was dissolved in H_2O_2 (30%) at 3ºC under ice bath to control the exothermicity. The requisite amount of this solution was used to impregnate on molecular sieves support, and the solution was slowly added to the support under constant stirring. The excess solution was evaporated and dried at 120ºC in air for 10 h followed by calcinations at 400ºC for 4 h in air. These samples were designated as VT1, VT2, VT3 and VT4 catalysts containing 2, 4, 6 and 8 wt% of vanadium respectively.

The above obtained samples were characterized for the N_2 BET surface area, X-ray diffraction, TPR, SEM and AAS analysis. N_2 adsorption–desorption isotherms were measured at -196°C on a Quantachrome Autosorb-1C, USA. The samples were first outgassed at 200°C under dynamic vacuum (10^{-2}Torr) for 8 h and then allowed to cool to a room temperature. Catalysts surface micrograms were obtained by FEI ESEM Quanta 400

instrument, USA equipped with ion sputter JEOL, JFC 1100 coating unit. Temperature Programmed Reduction (TPR) was performed on Micromeritics (ASAP 2920) sorption unit. To obtain the quantitative amount of Vanadia metal percent, AAS was carried out by atomic absorption spectrophotometer (GBC Avanta PM, Australia). X-ray diffraction patterns of calcined catalysts were recorded on PANalytical X-ray diffractometer.

B. Activity Studies

The vapor phase catalytic oxidation of ethyl acetate (EA) was carried out using a fixed-bed continuous flow reactor (6mm) interfaced with an online GC. The ethyl acetate (AR grade 99% Aldrich), nitrogen and air (Baruka Gases, India Ltd., 99.8%) gases were used in this study. The reaction was studied in the temperature range of 100-300ºC (for air) and 100-200ºC (for ozone). Samples form reaction product stream were introduced into the GC/FID (Thermo GC). Separation of the product stream was done by using factor four TM capillary column (15m x 0.25mm) for partial oxidation products and reactants. The CO and CO_2 were analyzed by CO (SR 94 electrochemical based detectors), CO_2 (IR based detectors P90 Technovation Analytical Instruments Ltd., India) sensors, respectively. The initial concentration of ethyl acetate was measured for each set of experiment by using a by-pass line. Qualitative analysis was done by GC-MS (Agilent 6890N) equipped with mass-selective detector using BP-10 (30m x 0.25mm). For air, Ethanol was the major product. For ozone, carbon oxides were the major product. Besides this, some trace of diethyl ether and methyl ester were also obtained.

3. RESULTS AND DISCUSSIONS

A. BET surface area

The BET surface areas of the V_2O_5 / mol. sev catalysts (Table 1) are in the range from 120 to 450 m^2/g catalyst. With increasing the vanadium loading the surface area goes through a maximum of 444 m^2/g at a vanadium loading of 2 wt% to 127 m^2/g (8 wt%). The decrease in the surface area is more pronounced at the lower loadings in case of vanadia catalysts (Chandra Shekar *et al.*, 2011). The catalyst pore size distribution (Fig. 1) reveals that the distribution is in narrow range and most of the area is in the mesoporous range which is ascribed to the mol sev support. However, at lower loadings still the mesopores are available on the catalysts and with increasing the vanadia loading, the complete mesopore volume is occupied by the vanadia. At higher loadings, the meso and macro pore volume also decreased due to the formation of larger vanadia particles and as a result the marginal variation in the surface area is observed.

B. X-ray Diffraction Analyses

The X-ray diffraction patterns of supported vanadia catalysts of 2% and 6% metal content are displayed in Fig. 2.

Li *et al.* (2006) in their studies reported the reflections consistent with the layered structure of hydrated V_2O_5 at $2\theta = 9.1, 18.3, 27.7, 37.2$ and 46.0^o are assigned

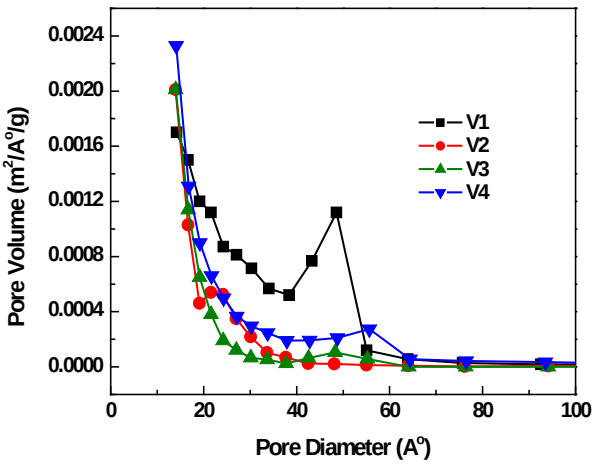

Fig.1. Pore Size Distribution Curve of V_2O_5 catalyst

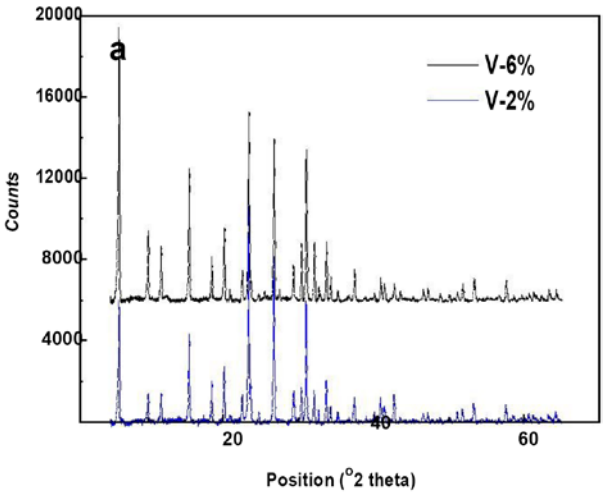

Fig.2. X-ray diffraction patterns of V/molecular sieves catalyst.

to (001), (002), (003), (004) and (005) lattice planes, respectively. XRD pattern of vanadia catalyst does not show any specific peak at these angles, in fact the XRD patterns indicate that V_2O_5 is in highly dispersed state. This can be due to the V_2O_5 crystallites are less than 5 nm which are below the XRD detection limits. The diffraction signals observed in the catalysts is attributed to the molecular sieve support. The calcined and used vanadia catalysts observed to be x-ray amorphous in natures for all the vanadia loadings.

C. Temperature Programmed Reduction (TPR)

TPR profile of the V-3 (6%V) catalyst is presented in Fig. 3. The V2O5 exhibited multiple reduction peaks in the temperature range from 300 to 800ºC (Machold *et al.*, 2008). The sharp peak at 430°C (low temperature LT) corresponds to the reduction of V_2O_5 to V_6O_{13}, and the second peak centered at 550°C is associated with the reduction of V_6O_{13} to V_2O_4.

D. Atomic Absorption Spectroscopy (AAS)

The catalyst sample (1 g) was used for the extraction of metal and was analyzed by atomic absorption spectrophotometer. The results obtained from the analyses are shown in the Table1.

Table 1: Catalyst Characterization

Catalyst	Theoretical wt.%	Metal % obtained from ASS	BETSA ($m^2 g^{-1}$)
V1	2	1.89	444
V2	4	3.76	395
V3	6	5.88	380
V4	8	7.73	127

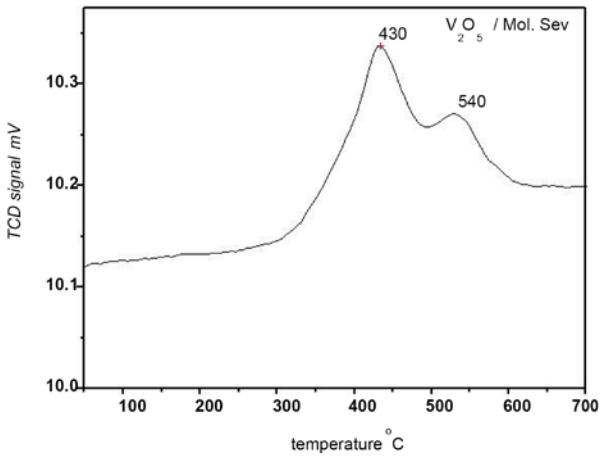

Fig. 3. TPR pattern of V/mol sev catalyst

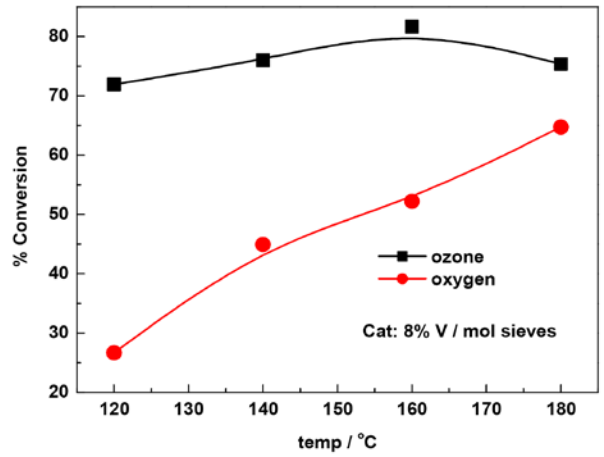

Fig. 4. Effect of reaction temperature on the decomposition of ethyl acetate.

E. Activity Studies

Effect of reaction temperature on EA decomposition in presence of air and ozone

Effect of reaction temperature on the conversion of ethyl acetate in presence of V/mol sieves catalyst with respect to the oxidants (air and ozone) is shown in the Fig. 4. As we can see that with air, on increasing the reaction temperature from 120ºC to 180ºC, the conversion of ethyl acetate increases continuously from 27% to 65%. While with ozone the conversion increases from 72% (at 120ºC) to 82% (at 160ºC) whereas it was seen that on further increasing the reaction temperature to 180ºC, the conversion value decreased to 75%. It appears that with increasing the reaction temperature, the surface decomposition of O_3 to oxygen is relatively increasing compared to the catalytic decomposition of O_3 and EA form ethanol (by hydrolysis) and CO_2. This observation was in line with the studies carried out earlier for ozone assisted partial oxidation of DMS to DMSO in presence of iron catalysts (Chandra Shekar *et al.*, 2009) and other similar studies (Mehandijev and Naidenov, 1992; Radhakrishnan and Oyama, 2001; Soni *et al.*, 2014).

Effect of Vanadium loading at various temperatures

Effect of vanadium loading on the decomposition of ethyl acetate at various temperatures is shown in Fig. 5. In the presence of air (Fig. 5a), increasing vanadium loading increases the conversion of ethyl acetate, thus among the V-1, V-2, V-3 and V-4, V-4 (8% V) shows higher activity. While in case of ozone (Fig.5b), V-4 shows higher activity at lower temperatures whereas V-3 (6% V) shows higher activity at higher temperatures i.e. above 160ºC. It can be explained again on the basis of same observation that with higher vanadium content the surface decomposition of ozone to oxygen increases relatively.

Effect of metal content on conversion and selectivity

The effect of vanadium loading on the conversion of ethyl acetate and product distribution in presence of air and ozone at 160ºC of reaction temperature is depicted in the Fig.6 a and b respectively.

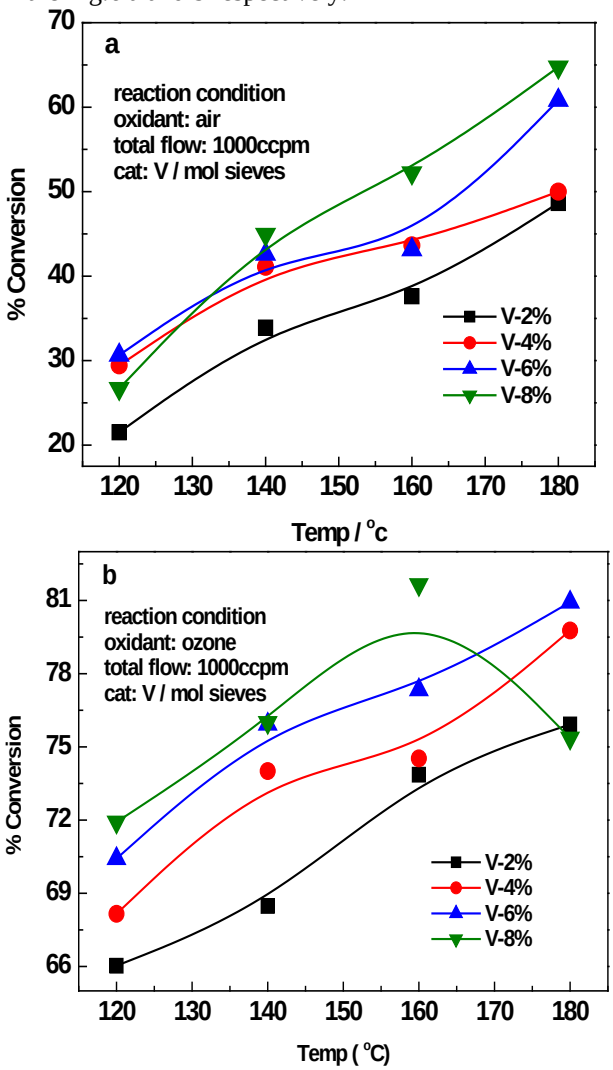

Fig.5. Effect of temperature on ethyl acetate decomposition over various metal contents (a) air and (b) ozone.

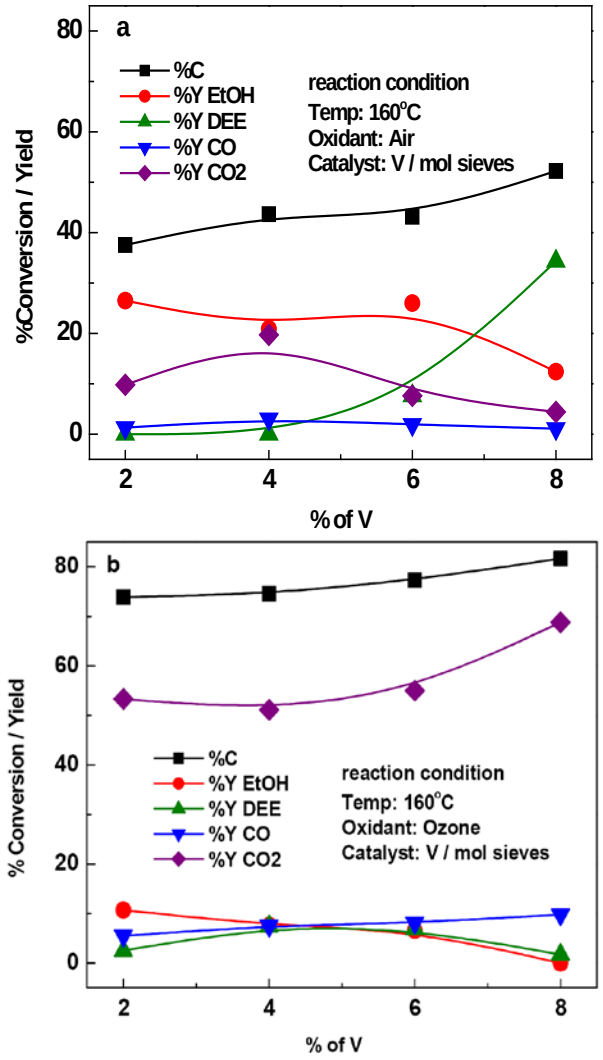

Fig.6. Effect of metal content on ethyl acetate decomposition (a) air and (b) ozone.

It was found that with air, on increasing the vanadium content from 2wt% to 8wt% at 160ºC temperature the conversion of ethyl acetate increases from 37.5% to 52.5%. Among the products obtained, up to 6% loading the major product was ethanol, while for 8% V, diethyl ether was found as the major product. This may be attributed to the fact that on increasing the vanadium content the conversion of ethanol into diethyl-ether increases due to more number of V-O-Si species which are selective for diethyl ether (Kannan *et al.*, 1991).

$$2\mathrm{EtOH} \xrightarrow{\mathrm{V-O-Si}} \mathrm{EtOEt} + \mathrm{H_2O}\,.$$

Under the same reaction conditions, with ozone it was found that on increasing the metal loading, the conversion of ethyl acetate increases marginally from 74% to 82%, and the major product found was carbon dioxide.

IV. CONCLUSIONS

When ozone is employed as oxidant, the decomposition of ethyl acetate is maximum at lower temperatures compared to the catalytic air oxidation. In presence of air, ethanol is the major product, while with ozone, CO_2 is the main product, thus we can say that ozone based oxidation converts ethyl acetate into TOP. The ozone assisted catalytic decomposition of ethyl acetate is promising for low VOCs and the byproduct formation is very minimal and complete mineralization is possible by tuning the process parameters.

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