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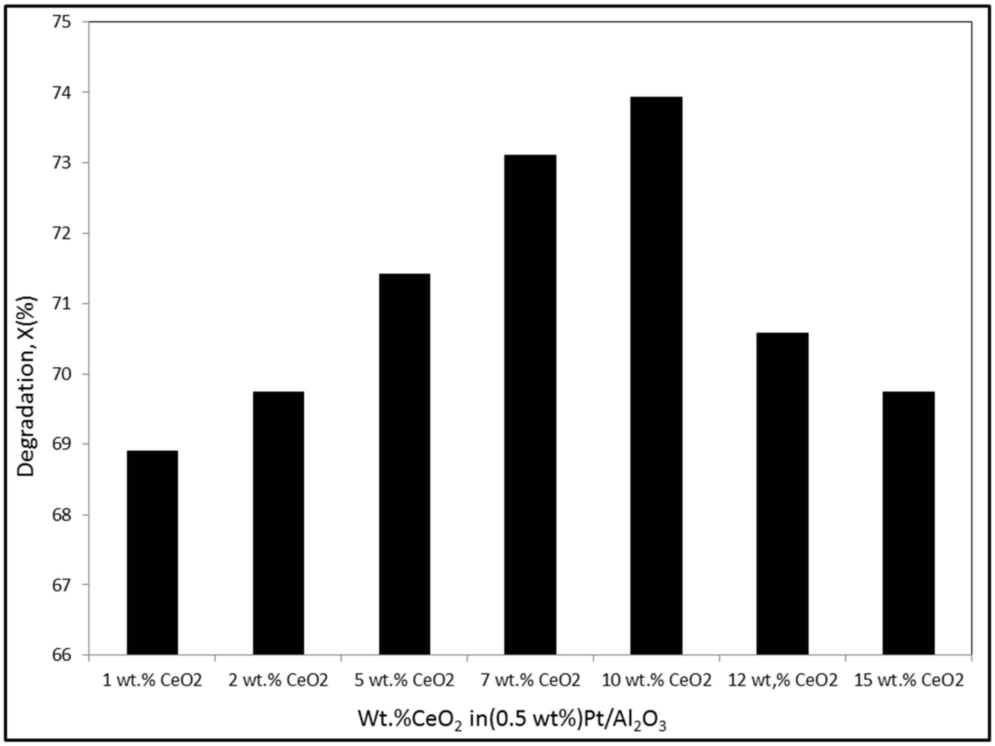

Graphical Abstract
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Ceria Promoted γ-Al_2O_3 Supported Platinum Catalyst for Catalytic Wet Air Oxidation of Oxalic Acid: Kinetics and Catalyst Deactivation

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Abstract: Alumina-supported platinum catalysts were prepared for catalytic wet air oxidation of oxalic acid. Addition of ceria as a promoter to alumina supported catalyst enhanced the catalytic activity, and significant conversions about 74 % were obtained at 363 K and atmospheric pressure. The long-term deactivation resistance of the ceria promoted Pt/Al_2O_3 catalyst is higher than that of the Pt/Al_2O_3 catalyst. A deactivation study of the catalysts was carried out using selective chemisorptions, X-ray powder diffraction (XRD) patterns and total organic carbon (TOC) analysis. The deactivation observed with the Pt/Al_2O_3 catalyst was attributed to the over oxidation of the surface of platinum by molecular oxygen and coke deposition on the catalyst surface.

Keywords: Pt/Al_2O_3 catalyst, ceria promoted Pt/Al_2O_3 catalyst, reaction kinetics, coke deposition, over oxidation.

1 Introduction

The increasing demand for the re-use of water and increasingly stringent water quality regulations lead to the need for treating all the different varieties of waste streams containing pollutants. This is particularly true for waters containing organic compounds such as waters discharged in chemical, petrochemical, textile or pharmaceutical processes. The inability of conventional methods to effectively remove many toxic organic pollutants has made it evident that new, compact and more efficient processes are needed.

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Several treatment technologies are available that can be used depending on the nature and volume of the effluent. Incineration is the most efficient useful method, but because of the high energetic costs involved and, above all, the release of noxious compounds (oxides of sulfur and nitrogen, furan) into the atmosphere, incineration is suitable only as an end-of-pipe treatment or when the chemical oxygen demand (COD) of the effluents is higher than 300 g/L. Biological treatment is a low cost and simple method, but the toxicity of the effluent makes this treatment ineffective for organic concentrations above 70-200 mg/L[1-3]. Potential technologies for COD removal between these two extremes include physicochemical treatment methods, air-based oxidation, and chemical oxidation. From the point of view of energy efficiency, wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) are suitable for wastewaters with low COD loads and within the given limits.[4, 5] Herbicide removal,[6] oxidative treatment of pulp and paper mill effluents[7, 8], pretreatment of waters from alkaloid plants (typically high-strength industrial wastewater with COD around 27 g/L) ,[9] treatment of printing and dyeing wastewaters from the textile industry,[10, 11] and treatment of H-acid manufacturing process effluents[12] are recent examples of applications of this technology.

In wet-air or thermal liquid-phase oxidation (WAO) process, the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures, is known to have a great potential for the treatment of effluents containing a high content of organic matter (chemical oxygen demand (COD) 10–100 g/L), or toxic contaminants for which direct biological purification is unfeasible.[13]

The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treated materials before they are released into the environment. This aqueous phase oxidation process takes place at high reaction temperatures (473–593 K) and pressures (20–200 bar) by means of hydroxyl radicals.[13] In WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralized into innocuous inorganic compounds such as CO_2, H_2O and inorganic salts, which remain in the aqueous phase. Sulphur is converted to sulphate, halogens to halides and phosphorus to phosphates. Organic nitrogen may produce ammonia, nitrate and nitrogen. In contrast to other thermal processes, WAO produces no NOx, SOx, HCl, dioxins, furans, fly ash, etc.[13]

One of the main drawbacks of the WAO process is its inability to achieve complete mineralization of organics, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in a wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide . Compared to conventional wet-air oxidation, catalytic wet-air oxidation (CWAO) has lower energy requirements. Due to the presence of a catalyst much higher oxidation rates are achieved and consequently, one can use less severe reaction conditions to reduce chemical oxygen demand to the same degree as in the case of noncatalytic process. In the CWAO process, organics are oxidized to innocuous inorganic compounds such as CO_2, H_2O and heteroatom dissolved ions at much lower temperatures and pressures than in uncatalyzed thermal processes.

By using a suitable catalyst, the operating conditions needed for the WAO process can be lowered to more amenable values (363-493 K, 1-50 bar) without loss of degradation efficiency and with consequent economic advantages.[14] Homogeneous catalysts are very efficient for the process,[15] but their use implies the need for an additional separation step in the process for the removal of the toxic ions from the solution. As heterogeneous catalysts are easily removed, their development and optimization has been the subject of several works in recent decades.[16-19]

Metals, metal oxides, and metal salts were used as catalysts for wet oxidation, like other oxidation reactions. Mixtures of metal oxide catalysts frequently exhibit greater activity than the single oxide. Co/Bi (5/1) catalyst[20] and Mn/Ce catalysts[21] showed good activity for the wet oxidation of acetic acid. Levec and Pintar[22] reported that CuO/ZnO/γ-Al_2O_3 catalyst (42/47/ 10 wt %) and CuO/ZnO/CoO catalyst (9.3/6.9/1.4 wt %) supported on steam-treated porous cement were effective for phenol oxidation. Supported noble metal catalysts are generally more active than metal oxides,[23] and many catalysts used in commercial wet oxidation processes are based on noble metals, especially platinum. Gallezot et al.[24] reported that platinum catalysts supported on active charcoal could be used under very moderate conditions to oxidize carboxylic acid. Hamoudi et al.[25] reported that Pt promotion of MnO2/CeO2 reduced the amount of carbonaceous deposits and improved phenol deep oxidation (higher CO2 yield). Taguchi and Okuhara[26] studied NH_3 oxidation over titania-supported platinum and palladium catalysts, and Pt/TiO_2 showed the superior activity of N_2 formation among other titania-supported noble metal catalysts.

There are several researches on the promoting effect of Ce for wet oxidation reactions. The promoting effect of Ce was reported for a Co/Bi catalyst, which was explained in terms of the variation in the electronic states of Co and Mn.[20] The promoting effect of Ce on mixed-metal oxides, CeO_2/ZrO_2/CuO and $CeO_2/ZrO_2/MnO_x$, for acetic acid oxidation was attributed to the enhancement of the redox properties of the active centers in the catalysts.[27] Zhang and Chuang[28] reported that Ce promoted the activity of an alumina-supported Pt catalyst but inhibited the activity of an alumina supported Pd catalyst for the wet oxidation of pulp mill wastes.

These studies mainly aimed at determining initial activities and kinetic parameters with attention being given to catalyst deactivation. The catalytic wet air oxidation of oxalic acid was investigated over alumina-supported Pt catalysts. The Ce addition effect on metal dispersion, the reducibility of catalysts, and the catalytic activity of the wet oxidation of oxalic acid was observed. Discussions were made on the factors affecting the activity of alumina-supported Pt catalysts by Ce addition.

Oxalic acid is a low molecular weight organic compound that is very refractory to oxidation, [29] it is a good model system because it occurs in most of the degradation pathways of more complex organic compounds. As expected, the conditions used in this process are quite favorable to the occurrence of various catalyst deactivation phenomena, such as poisoning, sintering, metal leaching into solution, and coke formation.[30, 31] In the present work, the deactivation of such catalysts is studied to determine their industrial applicability. Several experimental techniques are used in an effort to understand the deactivation mechanism, such as pulse chemisorptions (H_2 adsorption), scanning electron microscopy (SEM) analysis, thermo-gravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD) patterns and total organic carbon (TOC) analysis. A kinetic analysis describing the observed deactivation phenomena in the ceria promoted Pt/Al_2O_3 and Pt/Al_2O_3 catalysts were investigated using the experimental data obtained in the CWAO of the systems studied.

2 Experimental

2.1 Catalyst preparation and characterization

Platinum catalysts supported on alumina (Pt/Al_2O_3) and ceria promoted platinum catalysts were prepared by excess solution impregnation (ESI) method using preconditioned γ-Al_2O_3 as a support and H_2PtCl_6 .H_2O (CDH, India) and $Ce(NO_3)_2$.$6H_2O$(CDH, India) as metal precursors. Catalysts supported on alumina (Pt/Al_2O_3) with different Pt loadings (0.2 to 0.7 wt %) were prepared using preconditioned γ-Al_2O_3 support and hexachloroplatinic acid (CDH) as metal precursor. Double distilled water was used in all these experiments. The quantity of hexachloroplatinic acid required for the specific catalyst with pre-determined % Pt content was calculated from the stoichiometry. The amount of Pt solution of desired concentration was used for 10 g of alumina spheres and stirred continuously for 4 h. The excess water from the slurry was removed in a rotary vacuum evaporator at 80°C.The residue was then dried at 110°C for 24 h in an oven followed by calcination at 550°C in air for 4 h for complete decomposition of Pt oxide salts and deposition of the metal on the support structure.

The Pt/CeO_2-Al_2O_3 catalysts (containing 0.5 wt % Pt), with different CeO_2 contents (1, 2, 5, 7, 10, 12 and 15 wt %) were prepared with $Ce(NO_3)_2.6H_2O$ (CDH, India), $H_2PtCl_6.H_2O$ (CDH, India) and using preconditioned γ-Al_2O_3 support (10 g). The quantities of cerium nitrate and hexachloroplatinic acid required for the preparation of catalyst for specific Ce and Pt contents (% Ce and % Pt) were calculated using stoichiometry. The slurry of CeO_2-Al_2O_3 salts was stirred in a rotary vacuum evaporator for 4 h at 80^{o}C. The residue was then dried at 110°C for 24 h in an oven followed by calcination at 550°C in air for 4 h for complete decomposition of the nitrate to the support CeO_2-Al_2O_3. Pt was then impregnated on these supports using hexachloroplatinic acid to obtain 0.5 wt % Pt content, followed by drying and calcination at 550°C. Other batches of the catalysts were also prepared in a similar way using different weight % of ceria. The prepared catalyst was further reduced using H_2.

The specific surface area was obtained using the standard Brunauer-Emmett-Teller (BET) method by N_2 adsorption on AUTOSORB-1C micro pore surface area analyzer supplied by

Quantachrome, USA , while the pore size distribution was calculated from the adsorption branch of the isotherm by employing the Barrett-Joyner-Halenda (BJH) formalism and surface area of (0.5 wt %) Pt/Al_2O_3 and (0.5 wt %) Pt /(10 wt %)CeO_2-Al_2O_3 catalysts were found in the range of 138-172 m^2/g, total pore volumes were found in the range of 0.27-0.39 cm^3/g and pore diameters were found in the range of 8.0-9.1 nm. The hydrogen chemisorptions tests were carried out on Quantachrome Autosorb-1C and metal dispersion was calculated from the adsorption branch of isotherm by employing the strong/difference extrapolation formalism showed maximum number of active catalyst sites about 46-62% for Pt/Al_2O_3 catalysts and about 61-76 % metal dispersion for ceria promoted Pt/Al_2O_3 catalysts as ceria promotes dispersion of platinum metal. SEM and EDX analysis of fresh and spent catalysts were carried out with a Bruker-AXS Energy Dispersive X-ray (model Quantax 200) system, EVO-50 microscope. Thermo-gravimetric analysis (TGA) measurements were carried out in a high-resolution thermo-gravimetric analyzer (Seiko TG/DTA 32 SSC 5100). A 10-15 mg sample was loaded in a Pt pan, was heated from room temperature to 383 K, was kept at that temperature for 0.5 h, and then was heated to 973 K at the rate of 10 K/min. During this entire period air flow rate through the TGA furnace was maintained at 3 L/h. The change in the mass of the catalyst with temperature was recorded. X-ray powder diffraction (XRD) patterns were recorded on a Philips 1840 powder diffractometer using Cu-Kα radiation ($\lambda = 0.15418$ nm) at 40 kV and 45 mA in the range of $2\theta = 2^o$ to 80^o at a scanning speed in 2θ of 2^o per minute and a vertical goniometer at room temperature. It was found from X-ray diffraction (XRD) study that Pt crystal grains existed in the catalyst and the characteristic peaks were observed at $2\theta = 28.39°$ and 32.97°. Diffraction peaks at 56.29° and 66.91° confirmed the presence of Al_2CePt phase. The results matched with the JCPDS file 47-1612.The characteristic peak at 49.7°confirmed the presence of Ce, Pt crystallites in the catalysts as described by JCPDS file 19-0295. The platinum crystallite size was calculated using the half width of the Pt (111) peak by the Scherrer equation.

2.2 Oxidation measurements

The experiments were performed in a four-neck round bottom glass flask of 2 L capacity. During the experiment there was a possibility of water vapor escaping out of the flask at high temperature. This could lead to a change in the volume of the aqueous solution and can cause an error in calculating the concentration of oxalic acid. To avoid the escaping of water vapor from the flask, a condenser was placed at the top of the flask to reflux the water vapor. For a typical run, 1 L of oxalic acid solution with specified concentrations was taken in a glass reactor and the temperature of the reactor was kept constant at a desired value by the help of a temperature control unit. After reaching the desired temperature, 5 ml sample was taken with the aid of an automatic pipette to determine any change in oxalic acid concentration during the heating period. The corresponding time was recorded as the starting time of the reaction. Then catalyst at a given amount and air (which was a source of oxygen and passed from a compressor through a rotameter at constant flow rate of 2 L/min and oxygen was considered as excess in amount and oxalic acid was considered as a limiting reactant) were introduced immediately into the reactor while a magnetic agitator continuously stirred (400 rpm) the solution. The progress of the reaction was monitored by withdrawing samples from the flask at regular time intervals. The sample was titrated against 10^{-2}(M)NaOH solution using phenolphthalein as an indicator to determine the concentration of oxalic acid in the sample.

The percentage degradation of oxalic acid at any time t, namely oxalic acid conversion, was calculated using Equation 1

$$X(\%) = \frac{C_{OA\,0} - C_{OA}}{C_{OA0}} \times 100 \qquad (1)$$

where $C_{OA,0}$ is the initial concentration of oxalic acid and C_{OA} is the concentration of oxalic acid at any time t.

The material balance for oxalic acid was checked by measuring total organic carbon (TOC) in the samples using TOC analyzer (Analytic-jena, multi N/C-2100) the operation of which is based on combustion/non-dispersive infrared gas analysis. A close agreement between the degradation values of oxalic acid determined by titration method and TOC analyzer can be noticed. The oxidation of oxalic acid can lead to the formation of other carboxylic acids (acetic acid, formic acid). The oxalic acid samples (initial as well as withdrawn from the glass reactor after different time intervals of oxidation) were analyzed by HPLC (column: Nova-Pak C1-8 (Waters), 1ml/min flow rate of mobile phase (MeOH : H_2O : H_3PO_4 = 40 : 59.5 : 0.5 vol %) for the possible presence of other organic compounds other than oxalic acid. Only one peak was obtained for all the samples indicating the presence of only oxalic acid in the samples.

3 Results and discussion

3.1 Reaction Tests

Oxalic acid oxidation was first investigated (i) without catalyst and (ii) with the support without metal and it was found that, at 363 K and atmospheric pressure, the oxalic acid conversions after 5 h of reaction were 12 % and 17 %, respectively. For the same standard conditions but in the presence of the Pt/Al_2O_3 catalyst with a platinum metal load of 0.5 wt %, the conversion was 64 %, and it rose to 75 % in the presence of the ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalyst. The conversion curves followed the behavior described in Figure 1.

3.2 Effect of initial concentration of oxalic acid on degradation of oxalic acid

The effect of initial concentration of oxalic acid on the oxalic acid degradation over (0.5 wt %) Pt /(10 wt %)CeO_2-Al_2O_3 catalyst by performing experiments with different initial concentration of oxalic acid (500-3000 ppm) and the results are shown in Figure 2. It can be noticed that the initial reaction rate rises to a maximum for an initial oxalic acid concentration of 1500 ppm and then falls with further increasing initial concentration of oxalic acid above 1500 ppm. This indicates that surface reaction on two adjacent platinum active sites, based on Langmuir-Hinshelwood kinetics can be assumed to be the rate determining step in the concentration range of 500-3000 ppm oxalic acid, used in the present study. The competition between reactant molecules for active sites in catalyst particles resulted in decrease in the degradation of efficiency with increase in initial oxalic acid concentration from 1500-3000 ppm.

3.3 Effect of reaction temperature on oxalic acid degradation

The catalytic oxidation experiments were performed at different reaction temperatures to investigate the influence of reaction temperature on the oxidation of oxalic acid and the results are shown in Figure 3(a). An increase in oxalic acid degradation can be noticed with an increase in reaction temperature. This is due to the fact that the rate constant increases with an increase in the reaction temperature, leading to the enhancement of oxalic acid degradation since this process has been considered to be kinetically controlled. But the increase in the oxalic acid degradation was observed unto 363 K and further increase in the reaction temperature resulted in a decrease in the oxalic acid degradation. This could probably be due to the relatively lower adsorption of oxalic acid on the surface of catalyst at reaction temperature higher than 363 K.

Moreover, the solubility of oxygen decreases with an increase in temperature but the solubility of air in water is very low. Thus, an increase of reaction temperature results in an increase in the value of reaction rate constant of the kinetically controlled chemical reaction. However, the details of reaction mechanism are not revealed.

The activation energy of the reaction using (0.5 wt %) Pt/Al_2O_3 catalyst was found to be 47 kJ/mol while the activation energy using ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalyst was found to be 42 kJ/mol. The value of activation energy for ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalyst is lower than the (0.5 wt %)Pt/Al_2O_3 catalyst indicating higher activity of ceria promoted catalyst. The activation energies obtained in the present study are compared with the results reported in the literature and are tabulated in Table 1. It can be noticed that values of activation energies for oxalic acid obtained in the present study are roughly one-third of that obtained for WAO of oxalic acid. This is due to the fact that in the present study oxidation was carried out using a catalyst which facilitates a chemical reaction proceeds by a different pathway with a lower energy barrier. The activation energy determined in the present study is higher as compared to the value of activation energy reported by Gunduz and Dukkanci as the operating conditions are different in the two studies.[32]

3.4 Effect of loading of Pt (wt %) on oxalic acid degradation

Experiments were performed by varying the platinum content within the catalyst support by increasing the concentration of the hexachloroplatinic acid. A series of experiments were performed using the different Pt loading from 0.2 to 0.7 wt % and the results are shown in Figure 4. It can be noticed that there is an increase in oxalic acid degradation with the increase in loading of Pt from 0.2 to 0.5 wt %. It can be observed that maximum conversion (about 67 %) is obtained at 0.5 wt % loading of platinum metal and beyond 0.5 wt % Pt there is hardly any increase in the oxalic acid degradation. This may be due to the fact that enough active catalyst sites are available at 0.5 wt % catalyst loading for the reaction to occur and decrease in active catalyst sites due to higher catalyst loading will not enhance the reaction. The hydrogen chemisorption tests (Quantamchrome Autosorb-1C) showed maximum metal (67 % of 0.5 wt %

Pt) available for reaction in case of 0.5 wt % Pt loading (Table 2). Beyond the 0.5 wt % metal loading, metal available for reaction (54 % of 0.6 wt % Pt and 45 % of 0.7 wt % Pt) decreases due to either the pore of the catalyst support was blocked by metal precursor or agglomeration of metal in the case of higher loading of metal.

3.5 Effect of ceria loading in Pt/Al_2O_3 catalyst on oxalic acid degradation

Experiments were performed using different ceria amounts (1, 2, 5, 7, 10, 12 and 15 wt %) with the 0.5 wt % Pt loading to determine the optimum amount of ceria for the oxalic acid degradation and the results are shown in Figure 5(a). The degradation of oxalic acid was found to increase with an increase in ceria loading from 1 % to 10 wt %. The catalyst with 10 wt % ceria produced the best result, with 74 % conversion at a temperature of 363 K. A further increase in ceria loading beyond 10 wt % had a negative effect on the catalyst activity, leading to a decrease in the degradation of oxalic acid. This may be due to the reduction in the number of active catalyst sites. The graphs for % degradation of oxalic acid versus wt % of Pt in Pt/Al_2O_3 and Pt/(10 wt %)CeO_2-Al_2O_3 catalysts have been shown in Figure 5(b).

The hydrogen chemisorption (Quantamchrome Autosorb-1C) results from Table 3 showed that dispersion of Pt is maximum about 76 % with ceria loading 10 wt % as ceria promotes dispersion of Pt, and that strong Pt-ceria interactions may have a profound effect on the oxygen storage capacity.[33] Kim and Ihm reported that Pt seemed to be largely dispersed at lower ceria loading (under 10 wt %), and a Pt-Ce-Al_2O_3 interaction may exist.[34] The platinum crystallite size was calculated from Figure 5(c) and Figure 5(d) using the half width of the Pt (111) peak in XRD curve of the catalyst by the Scherrer equation (Table 4) and error of Pt particle size was found ±3%. From Table 4, we find that the Pt crystallite size on Pt/CeO_2-Al_2O_3 is smaller than that on Pt/Al_2O_3, which indicates that ceria can decrease the Pt crystallite size and inhibit Pt crystallite growth during reaction. The strong interaction between Pt and ceria may result in a larger extent of boundary area between cerium oxide and platinum and the active sites involve both Pt and ceria. It was found that during the CWAO process, some of the cerium was in the state of Ce (III).[35] The lower-valance-state cerium may dissociatively adsorb oxygen or water, and the resulting ad-species-O or –OH may be transferred to adjacent platinum and reacted with surface carbon species (HOOC-COOH) to give out CO_2 and H_2O. Zhuang[36] reported that cerium oxide itself oxidize hydrocarbon although its activity is several orders lower than other transition metal oxide, however, when noble metals coexist with cerium oxide, the reaction will be much accelerated. So the activity of Pt/CeO_2-Al_2O_3 catalyst increased. When the amount of ceria was increased beyond 10 wt % on the surface of catalyst, Ce (III) ion which is rich in electrons interacts with Pt atom, making Pt atom more electron enriched, therefore the degradation activity of Pt for oxalic acid is decreased.

The conversions obtained with the (0.5 wt %) Pt/(10 wt %) CeO_2-Al_2O_3 and (0.5 wt %) Pt/ Al_2O_3 catalysts are far higher than those obtained with the bare support, confirming the catalytic effect. By determining the metallic contents of the catalysts before and after 5 h reaction, it was concluded that almost no metal leaching occurred with these catalytic systems (Table 5). Noble metals are thermodynamically stable in the zerovalent state in a very broad range of conditions and specifically at the conditions employed in this work, thus leading to the absence of leaching. For deactivation analysis, the catalysts were recovered by filtration from the solution after reaction, washed with water, dried, and reused in successive runs with fresh oxalic acid solution. The results obtained are presented in Figure 6.

Several works have reported catalyst deactivation due to coke deposition on the catalyst surface, blocking the pores.[30] The Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts were texturally characterized before and after reaction by analysis of their N_2 adsorption isotherms. A slight loss in the catalysts specific surface areas and micropore volumes (Table 6) was observed after reaction, indicating the possibility of slight coke deposition.

The activity of the (0.5 wt %) Pt/Al_2O_3 and (0.5 wt %) Pt/(10 wt %)CeO_2 -Al_2O_3 catalysts was plotted against time and the results are shown in Figure 7. It can be noticed that the activity of the catalysts decreased significantly with time due to the catalyst decay. The oxalic acid degradation values presented in Figure 1 permits to build the activity–time curve shown in Figure 7. As observed, in the first 5 h of on reaction time of a deactivation experiment in isothermal conditions at 363 K, the catalyst activities are approximately 75 % and 87 % decreased for (0.5 wt %) Pt/(10 wt %)CeO_2 -Al_2O_3 and (0.5 wt %) Pt/Al_2O_3 catalysts respectively. However, on the following time interval the rate of deactivation becomes much smaller, appearing a trend of stabilization. The resulting time evolution of catalyst activity is presented by the points appearing in Figure 7. It was found that deactivation of catalysts followed first order kinetics for (0.5 wt %) Pt/(10 wt %) CeO_2 -Al_2O_3 and (0.5 wt %) Pt/Al_2O_3 catalysts.

The SEM analysis of the fresh and spent (0.5 wt %) Pt/Al_2O_3 and (0.5 wt %) Pt/(10 wt %) CeO_2 -Al_2O_3 catalysts was performed and it was found that some deposition blocked the active sites of the catalysts. The EDX analysis of the fresh and spent (0.5 wt %) Pt/Al_2O_3 and (0.5 wt %) Pt/(10 wt %) CeO_2 -Al_2O_3 catalysts was performed and the carbon peaks were found in addition to alumina (Al), platinum (Pt), cerium (Ce) and oxygen in the spent catalysts due to the traces of carbon deposition on the surface of the catalysts or pore mouths of the catalysts as it was also confirmed by TGA and TOC analysis that oxalic acid degradation decreases on account of carbon deposition on the surface of the catalysts.

The quantitative analysis of spent (0.5 wt %) Pt/Al_2O_3 catalyst on EDX showed that it contains C: 3.34 in wt % besides Pt: 0.41, Al: 44.64, O_2: 51.61 in wt %. But in fresh catalyst no carbon peak was observed. On the other hand, the quantitative analysis of spent ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalyst on EDX showed that it contains C: 1.16 in wt % besides Pt: 0.48, Ce: 6.73, Al: 40.83, O_2: 50.80 in wt %. But in fresh catalyst no carbon was observed. It was also observed that ceria reduces the coke deposition on the catalyst surface as carbon deposition decreases from 3.34 wt % to 1.16 wt % in spent ceria promoted (0.5 wt %) Pt/(10 wt %) CeO_2-Al_2O_3 catalyst compare to spent (0.5 wt %)Pt/Al_2O_3 catalyst. Tiernan and Finlayson[37] reported that ceria prevents sintering of surface metal precursors and reduces carbon deposition on the metal surface. The explanation anticipated for the difference in activity observed between the (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 and (0.5 wt %)Pt/Al_2O_3 catalysts is based on the reduction potentials of the respective metals. As platinum alone has a lower reduction potential than ceria promoted platinum catalysts, its surface has a higher propensity for oxygen adsorption.[38, 39] Oxygen will compete with oxalic acid for adsorption at the metal active sites. Compared with the ceria promoted platinum catalyst, the platinum catalyst will have fewer active sites available for oxalic acid adsorption, the first step in the oxalic acid oxidation reaction mechanism, and thus, it will exhibit lower activity. The quantitative analysis of fresh and spent Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts by EDX showed that the cause for metal deactivation in oxidation reactions is the poisoning of the metallic surface by oxygen (Table 7), accompanied sometimes by the irreversible adsorption of reaction products.[40] Oxygen tends to partially cover the metal by chemisorption, forming strong M-O (or M-OH) bonds.[41] In the case of ceria promoted platinum catalysts, the formation of PtO_2 and or PO_4 was also suggested and was confirmed by hydrogen titration experiments. [33] Both mechanisms of deactivation are reversible, allowing for catalyst partial reactivation by exposure to a nitrogen stream.[42] Surface coverage by oxygen depends on the relative affinity of the metal for oxygen, but in the presence of an organic substrate, competition has to be taken into account. The dynamic balance of the competitive adsorption between oxygen and the substrate controls the initial reaction rate and the reaction progress. The balance favors higher oxygen coverage as the concentration of the substrate in solution decreases, thus lowering the reaction rate. Total or partial catalyst deactivation is interpreted in terms of the over oxidation of the metallic surface,[42] a high oxidation activity being obtained when the competitive adsorption between oxygen and the organic substrate at the metallic surface is equilibrated. Some results from the literature reveal the existence of strongly adsorbed reaction products that block partially the surface, producing a genuine deactivation, which, when combined with over oxidation, results in a much higher deactivation rate.[43] A similar mechanism of oxygen deactivation can be considered in the case of the platinum catalyst. More study on over oxidation of metal will be carried out in future.

The Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts were texturally characterized before and after reaction by analysis of their N_2 adsorption isotherms. A slight loss in the catalysts specific surface areas and micropore volumes (Table 6) was observed after reaction, indicating the possibility of slight coke deposition. Several works have reported catalyst deactivation due to coke deposition on the catalyst surface[30] blocking the pores.

The thermo-gravimetric analysis (TGA) of the spent catalysts were carried out separately for spent (0.5 wt %) Pt/Al_2O_3 and ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2 -Al_2O_3 catalysts and it can be noticed that there is a significant weight loss during the initial heating up period in the temperature range 373-573 K. This weight loss is mostly due to the removal of the moisture content on the catalyst surface and retained inside the pores, which necessitated somewhat higher temperature to remove the excess moisture. Part of weight loss could also be due to the removal of easily oxidizable carbonaceous species like amorphous carbonformed during initial decomposition of oxalic acid. Moreover, the water bonded with the catalyst requires higher temperature for desorption. Further increase in temperature did not lead to any significant change in the weight of the sample, which confirms that there was no trace of any carbon deposition on the surface of the catalyst.

Total organic carbon (TOC) analysis of spent (0.5 wt %) Pt/Al_2O_3 and ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2 -Al_2O_3 catalysts was carried out using Analytic Jena N/C 2100, HT1300 Solids module analyzer at 1473K and oxygen flow rate of 2.5 L/min. It was found that 3.34 wt % and 1.16 wt % carbon was present in spent (0.5 wt %) Pt/Al_2O_3 and ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalysts respectively and 0.33 wt % and 0.17 wt % carbon was present in regenerative (0.5 wt %) Pt/Al_2O_3 and ceria promoted (0.5 wt %) Pt/(10 wt %)CeO_2-Al_2O_3 catalysts respectively.

The catalyst was regenerated by burning it an stream of air at 550ºC for 5h.The catalyst was reduced by hydrogen and used only one time after regeneration and it was found that there was a 2% reduction in oxalic acid degradation for ceria promoted (0.5 wt%)/(10 wt%)CeO_2-Al_2O_3 catalyst. No repeated use (more than one) of the catalyst was made.

4 Conclusions

The alumina-supported platinum (Pt/Al_2O_3) and ceria promoted platinum (Pt/CeO_2-Al_2O_3) catalysts prepared in this work are very efficient in oxalic acid removal by CWAO. The prepared catalysts are very stable under the reaction conditions, with no significant leaching of the metal phase being observed. The ceria promoted platinum catalysts are more resistant to deactivation than the corresponding platinum catalysts. Blockage of the pores by coke deposition was observed. Metal sintering is also not likely to occur significantly under the reaction conditions. The platinum catalyst undergoes deactivation due to over oxidation of the metal surface in a mechanism similar to that ascribed to the ceria promoted platinum catalysts. The reaction kinetics and catalyst deactivation study are of practical interest for the design of continuous catalyst systems, accounting for the description of mechanistic aspects of catalyst deactivation in CWAO.

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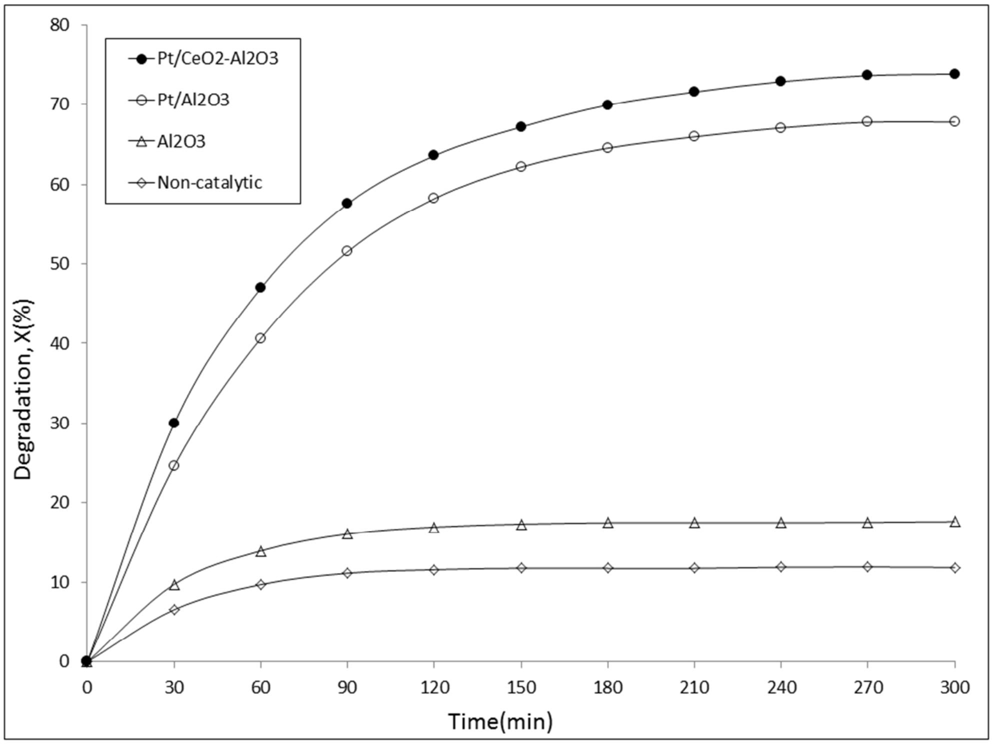

Figure 1. Noncatalytic, with support without metal and with metal degradation of oxalic acid.
Temperature:363 K, Pressure: Atmospheric, Agitation Speed: 400 rpm.
254x190mm (96 x 96 DPI)

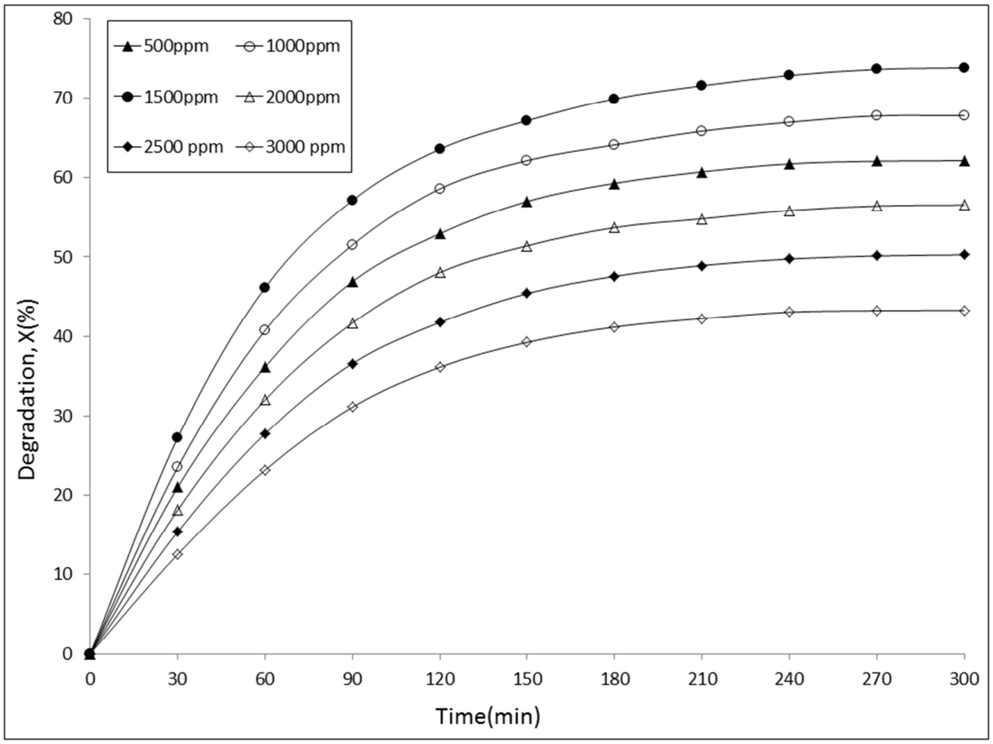

Figure 2. Effect of initial concentration of OA on degradation using (0.5 wt%)Pt/ (10 wt %) CeO2-Al2O3catalyst. Air flow rate: 2 L/min, Catalyst dosage: 1 g/L, Temperature: 363 K, Agitation: 400 rpm, Catalyst size:45-75μm.

254x190mm (96 x 96 DPI)

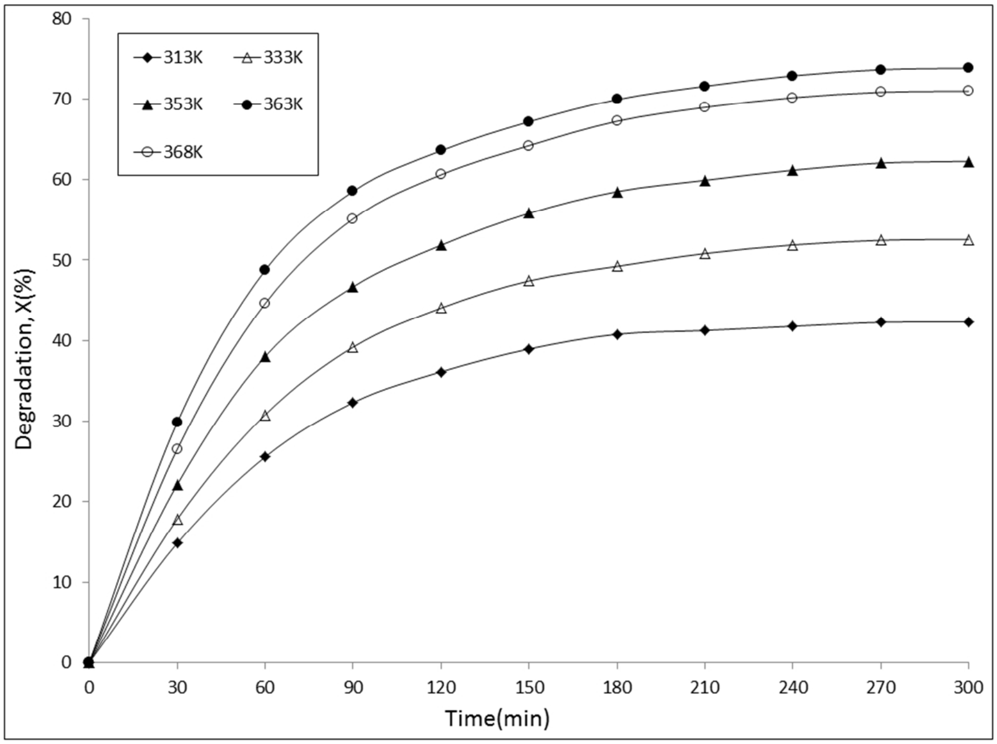

Figure 3(a). Effect of temperature on degradation using (0.5 wt%)Pt/(10 wt%) CeO2-Al2O3 catalyst.Initial concentration: 1500 ppm, Air flow rate: 2 L/min, Catalyst dosage: 1 g/L, Agitation: 400 rpm,Catalyst size: 45-75 μm.
254x190mm (96 x 96 DPI)

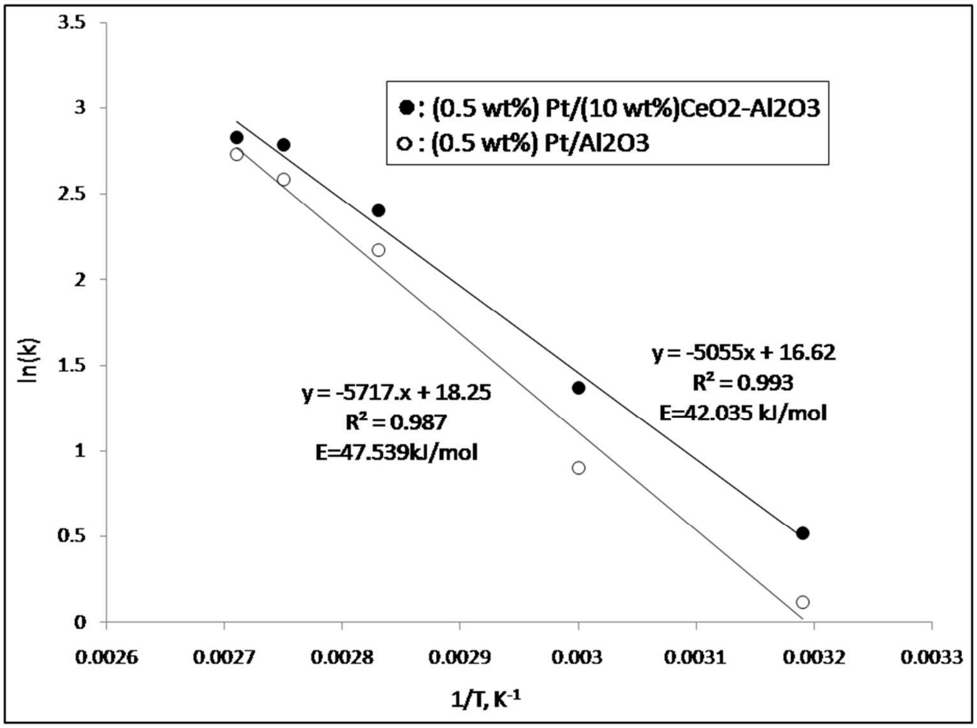

Figure 3(b) Arrhenius plot of ln (k) as a function of 1/T for (0.5 wt %)Pt/Al2O3 and (0.5 wt%)Pt/(10 wt%)CeO2-Al2O3 catalysts.
254x190mm (96 x 96 DPI)

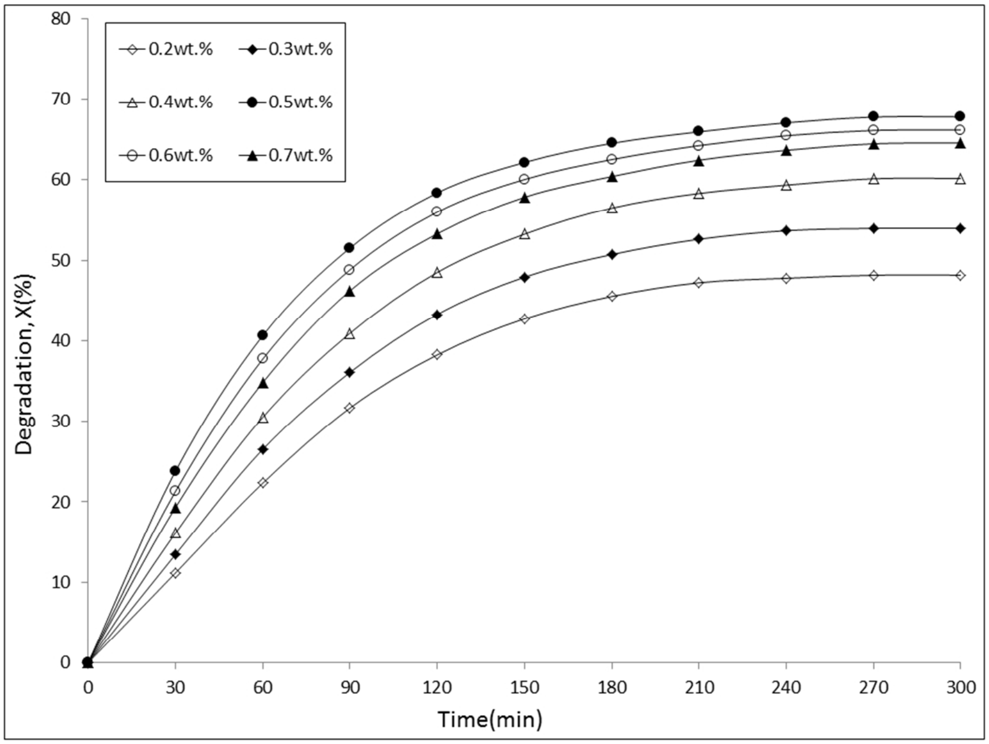

Figure 4. Effect of loading of Pt on OA degradation.Initial concentration: 1500 ppm, Air flow Rate: 2 L/min, Catalyst dosage: 2 g/L, Temperature: 363 K, Agitation: 400 rpm, Catalyst size: 45-75μm.

254x190mm (96 x 96 DPI)

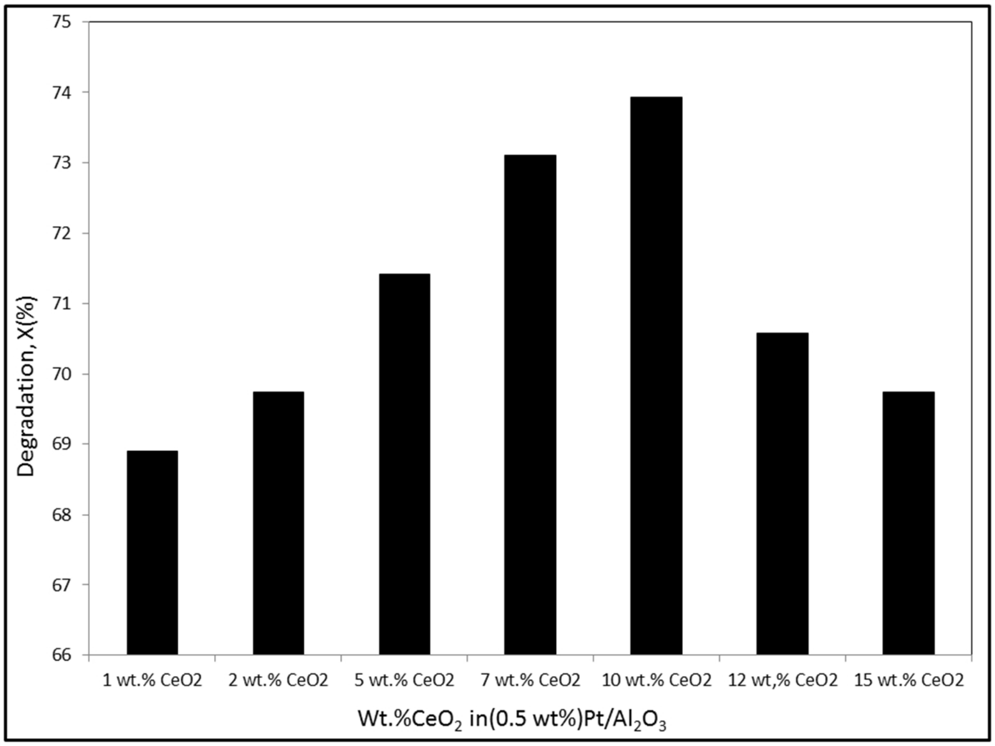

Figure 5(a). Effect of ceria loading on OA degradation.Initial concentration:1500 ppm, Temperature:363 K, Air flow rate:2 L/min, Catalyst dosage:1 g/L, Agitation: 400 rpm, Catalyst size:45-75 µm.

254x190mm (96 x 96 DPI)

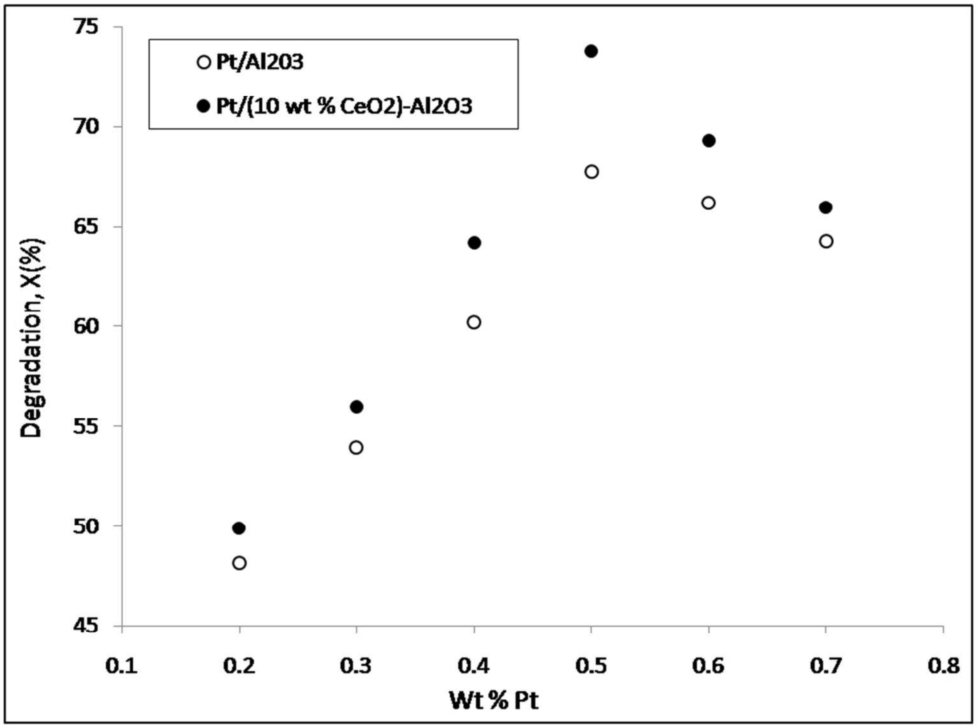

Figure 5(b). Graph for % degradation of oxalic acid vs. wt % of Pt in Pt/Al2O3 and Pt/(10 wt %)CeO2-Al2O3.

254x190mm (96 x 96 DPI)

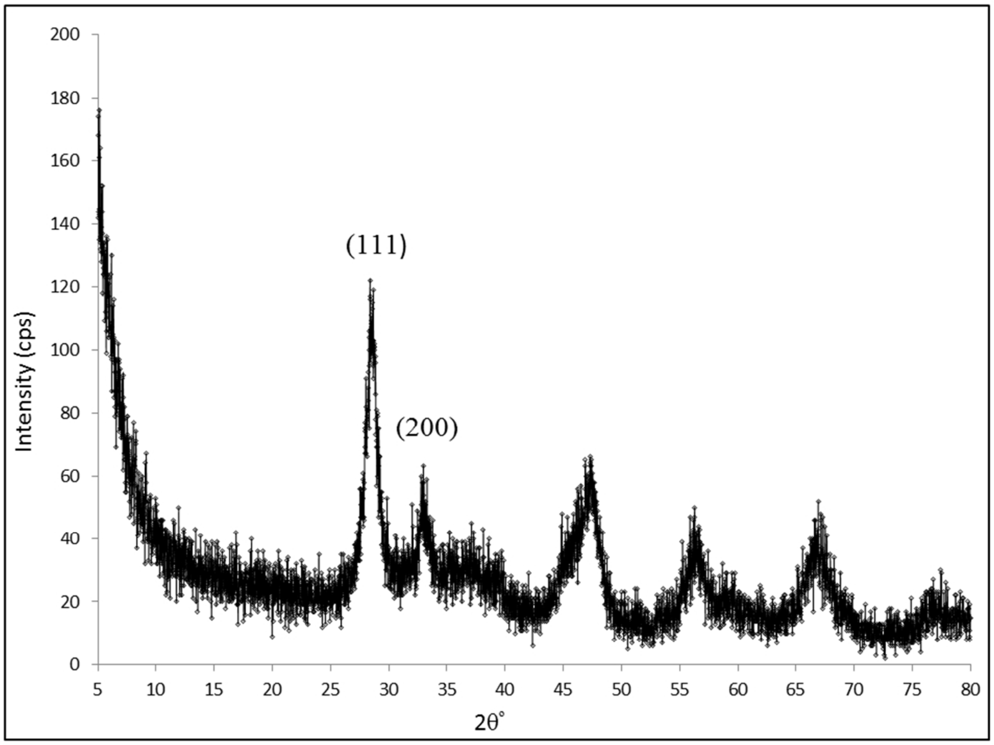

Figure 5(c). XRD plot for Pt(0.5 wt%)/CeO2(10 wt%)- Al2O3 catalyst
254x190mm (96 x 96 DPI)

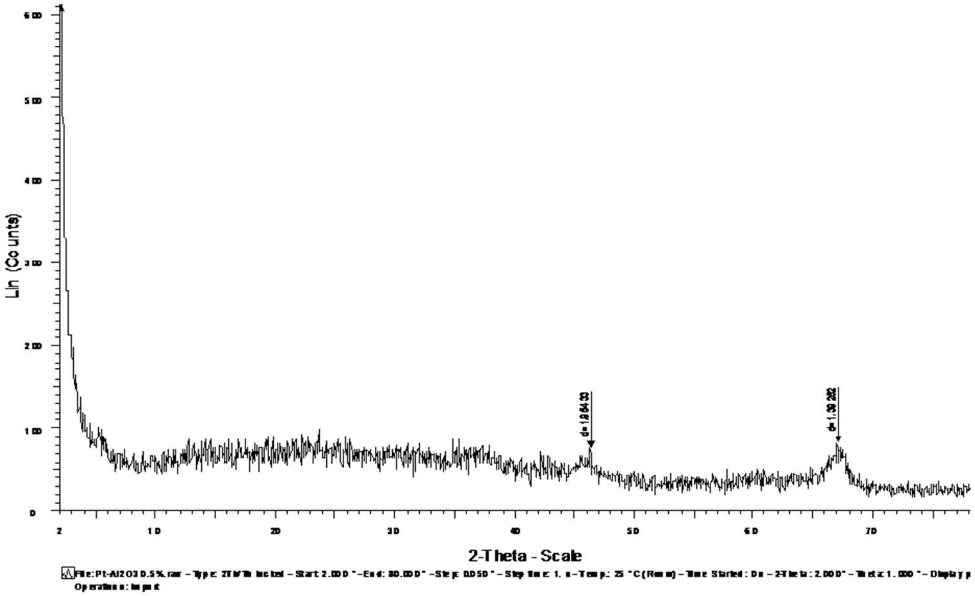

Figure 5(d) XRD plot for Pt(0.5 wt%)/Al2O3 catalyst
254x190mm (96 x 96 DPI)

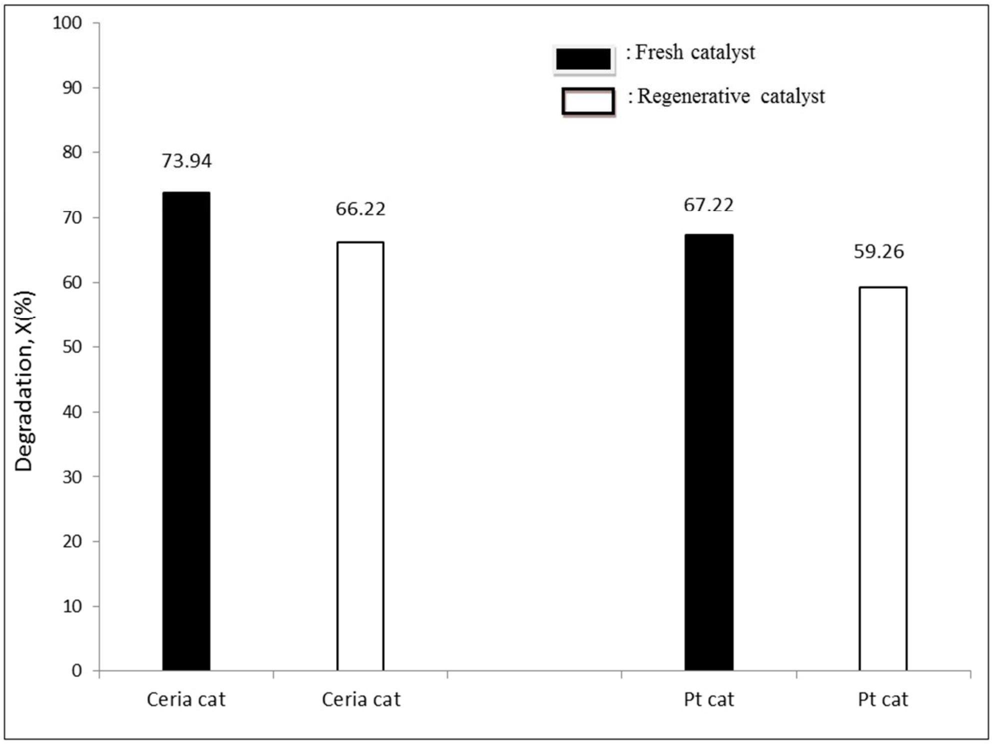

Figure 6. Degradation curves obtained in consecutive oxidation runs of fresh oxalic acid solutions at 363 K and atmospheric pressure using fresh and regenerative (0.5 wt%)Pt/Al2O3 and ceria promoted (0.5 wt%)Pt/(10 wt%) CeO2-Al2O3 catalysts.
254x190mm (96 x 96 DPI)

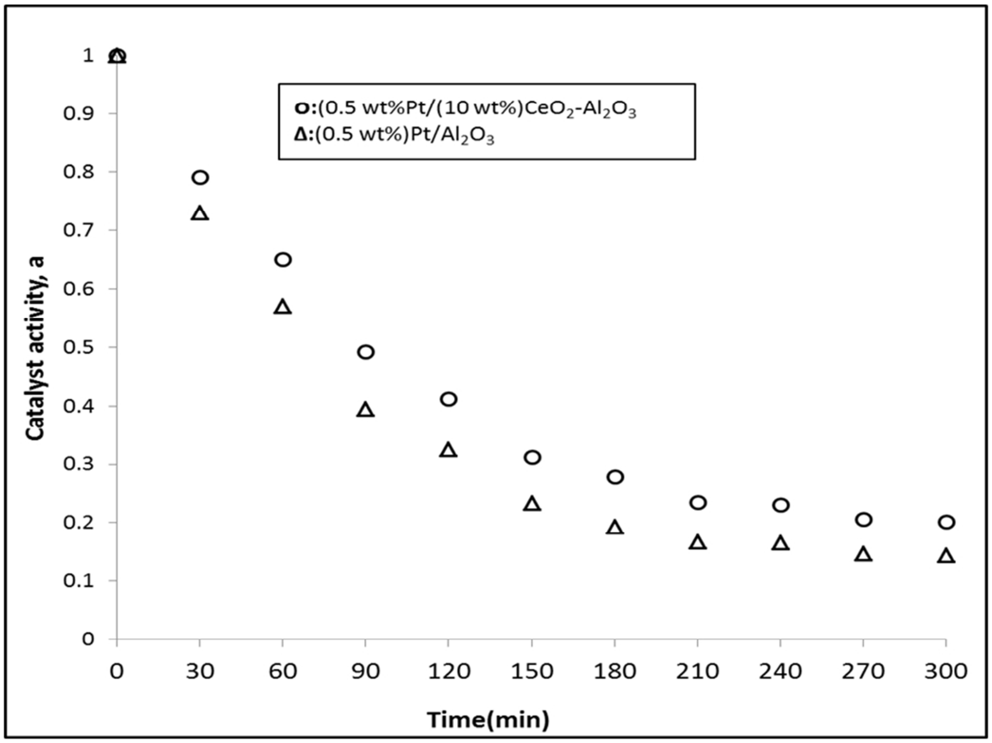

Figure 7. Plot for catalyst activity as a function of time using (0.5 wt%)Pt/(10 wt%)CeO2-Al2O3 and (0.5 wt%) Pt/Al2O3 catalysts.

254x190mm (96 x 96 DPI)

Figure Caption

Figure 1.Noncatalytic, with support without metal and with metal degradation of oxalic acid. Temperature:363 K, Pressure: Atmospheric, Agitation Speed: 400 rpm.

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Figure 5(b). Graph for % degradation of oxalic acid vs. wt % of Pt in Pt/Al_2O_3 and Pt/(10 wt %)CeO_2-Al_2O_3.

Figure 5(c). XRD plot for Pt(0.5 wt%)/CeO_2(10 wt%)- Al_2O_3 catalyst

Figure 5(d) XRD plot for Pt(0.5 wt%)/Al_2O_3 catalyst

Figure 6. Degradation curves obtained in consecutive oxidation runs of fresh oxalic acid solutions at 363 K and atmospheric pressure using fresh and regenerative (0.5 wt%)Pt/Al_2O_3 and ceria promoted (0.5 wt%)Pt/(10 wt%) CeO_2-Al_2O_3 catalysts.

Figure 7. Plot for catalyst activity as a function of time using (0.5 wt%)Pt/(10 wt%)CeO_2-Al_2O_3 and (0.5 wt%) Pt/Al_2O_3 catalysts.

Table 1. Calculated activation energies in comparison with data reported in literature

Author	Compound	Activation Energy (kJ/mol)	Reference
Gunduz & Dukkanci	Oxalic Acid	24.6	[32]
Shende & Levec	Oxalic Acid	137	[44]
Shende & Mahajani	Oxalic Acid	129.4	[45]
Foussard	Oxalic Acid	133.8	[46]
Present study using (0.5 wt %) Pt/Al2O3	Oxalic Acid	47	
Present study using (0.5 wt %)Pt/(10 wt%) CeO_2-Al_2O_3	Oxalic Acid	42	

Table 2. Chemisorptions results for Pt/Al_2O_3 catalysts

Pt metal loading	Pt metal dispersion
0.2	71.5
0.3	69.5
0.4	69.0
0.5	67.0
0.6	54
0.7	45

Table 3: Chemisorptions results for ceria promoted Pt/Al_2O_3 catalysts

Ceria loading (wt%)	Pt loading (wt%)	Pt metal dispersion (%)
1	0.5	68.55
2	0.5	70.25
5	0.5	72.46
7	0.5	74.27
10	0.5	75.72
12	0.5	65.77
15	0.5	61.38

Table 4. Pt crystallite sizes of catalysts before and after 5 h reaction

Ceria loading (wt %)	Pt particle size (Å) before reaction	Pt particle size (Å) after reaction
0	21.0	28.0
1	11.5	12.1
2	9.0	9.2
5	8.5	8.6
7	8.3	8.7
10	8.0	8.3
12	7.8	8.1
15	7.5	7.9

Table 5. Metal contents of the catalysts before and after reaction

Catalyst	Pt metal loading (wt %)	Pt metal content before reaction (wt %)	Pt metal content after reaction (wt %)
Pt/Al_2O_3	0.5	0.34±0.02	0.34±0.015
Pt/CeO2-Al_2O_3	0.5	0.38±0.025	0.38±0.022

Table 6. Catalyst textural characterization before and after reaction

Catalyst	BET surface area before reaction (m^2/g)	BET surface area after reaction (m^2/g)	Pore volume before reaction, V(cm^3/g)	Pore volume after reaction, V(cm^3/g)
(0.5 wt %) Pt/Al_2O_3	125	111	0.30	0.27
Ceria promoted (0.5 wt %) Pt/(10wt %) CeO_2-Al_2O_3	120.5	112	0.26	0.24

Table 7. Carbon and oxygen content of the catalysts before and after reaction

Catalyst	Carbon present in before reaction (wt %)	Carbon present in after reaction (wt %)	Oxygen present in before reaction (wt %)	Oxygen present in after reaction (wt %)
Pt/Al_2O_3	-	3.34	49.12	51.61
Ceria promoted Pt/Al_2O_3	-	1.16	48.98	49.20