

ALTERNATIVE DESTRUCTION TECHNOLOGY OF VOLATILE ORGANIC COMPOUNDS IN AIR USING ACTIVATED CARBON

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ABSTRACT

In air, volatile organic compounds (VOCs) like benzene, toluene and xylene exist in very small amount. Thus, recovery is not an economical option. Adsorption using activated carbon and catalytic oxidation are two of the most common methods employed in the control of VOC emission. The combination of these two technologies, on the other hand, proves to be advantageous in the destruction of VOCs at low temperature.

Activated carbon locally produced from coconut shell (AC1) and a commercial activated carbon (AC2) had been characterized and used in the adsorption and catalytic oxidation of volatile organic compounds. By Temperature Programmed Desorption, the breakthrough volume of AC1 has been measured to be only a fourth of that of AC2. This was confirmed by BET surface area measurement. Ignition temperature of AC1 is 250°C while that of AC2 is 300°C.

CeO₂ supported on activated carbon catalysts were prepared by impregnation method. During xylene oxidation with oxygen at 50-100°C, xylene reduction is due to adsorption on the AC while at higher temperatures, xylene oxidation on ceria takes place. All catalysts show moderate activity in terms of xylene conversion while selectivity to CO₂ is 100 percent. Highest CO₂ yield is obtained with 15% ceria loading.

By characterizing the activated carbon and the conduct of activity test on the catalysts, improvement of AC may be done. At the same time, better metal oxide may be used alone or together with cerium oxide for higher oxidation activity at even lower temperature.

INTRODUCTION

Volatile organic compounds or VOCs are one of the hazardous pollutants found in air. VOCs in air exceeding the tolerable concentration limits have been investigated to generally cause mutagenic, carcinogenic, or teratogenic effects to humans. These compounds are likewise precursors to photochemical smog, which has adverse effects to the environment and to life forms as well [1].

The main sources of exposure to VOCs from indoor air are consumer products, building materials, and personal activities. Chemical plants, petroleum refineries, automobiles, and hazardous waste sites, meanwhile, serve as traditional outdoor sources of VOCs. VOC exposure is associated with several human activities such as smoking, driving, taking

showers, cooking, painting, varnishing, automobile refueling, and photocopying. On the other hand, VOCs may also come from building materials including adhesives, lubricants, fabrics, rubber, paint, wall and floor coverings, solvents, thinners, degreasers, cleaners, liquid fuels, and others. These organics are also among the most common pollutants being emitted by the chemical process industries [2]. Specifically, VOCs emanate from wastewater treatment operations, storage vessels, process vents, and transfer operations.

The ever-escalating stringency of the regulatory requirements regarding control strategies for VOC emissions is the driving force behind the development of and continuing research for VOC abatement technology enhancements and modifications.

TECHNOLOGIES FOR VOC CONTROL

To date, abatement technologies for VOCs can be classified as either recovery or destruction devices. Generally, solvent recovery is a logical consideration for any industrial process emitting large quantities of valuable solvent [3] while the latter is practically applied to treat the surrounding air contaminated with relatively minute amounts of organic pollutants [4].

Recovery of VOCs involves the regeneration of the organic compounds for reuse, most commonly, by the adsorption and desorption processes using activated carbon. Activated carbons are excellent adsorbents and are used to purify, decolorize, filter, remove or separate one component from another [5]. Adsorption through activated carbon is proven to be a very suitable, effective and economical means of controlling VOC emissions in air. The excellent adsorption properties of activated carbon are essentially attributed to their large surface area, high degree of surface reactivity, and vast infrastructure of pores and micropores, which makes the internal surface accessible, enhances the adsorption rate and increases the saturation capacity.

Aside from VOC recovery by adsorption, other destruction technologies are available and some are still being developed or improved. This is due to more stringent regulations to improve air quality. Destruction devices entail the thermal or catalytic oxidation of these air-polluting compounds to harmless carbon dioxide and water [6]. Between the two types of VOC oxidation process, the catalytic oxidation proves to be more advantageous than the thermal combustion process. This is because VOC oxidation over a catalyst proceeds faster, and allows a lower operating temperature for the same amount of conversion with that in the thermal process. This translates to improved economics for fuel consumption and reduced expenses for reactor construction materials, since corrosion is minimized.

Catalytic materials employed in the oxidation of VOCs are generally the base metal oxides (e.g. Cr_2O_3), precious metals (e.g. Pt and Pd) and combinations of both [7]. Supported noble metals, especially Pt and/or Pd dispersed on carriers, are known to dominate the VOC oxidation catalysts with their high activity; good poison resistance, ability to be regenerated, and thermal durability [8]. However, these catalytic materials, because of their rarity, high demand for environmental and industrial applications, and thus, expensiveness, may prove to be unsuitable to developing countries like the Philippines. Nevertheless, studies [9, 10, 11] have investigated and proven the good catalytic performance of possible alternatives to noble

metals – supported metal oxides – in oxidizing harmful organics. One of the metal oxides utilized for oxidation is alumina-supported ceria, which has been proven in a study conducted by the DLSU's Environmental Engineering Laboratory to be a promising oxidation catalyst of hydrocarbons, as well as carbon monoxide, from automobile exhaust emissions.

On the other hand, a study [12] has demonstrated the benefits of combining the processes of adsorption (using activated carbon or other adsorbents), and catalytic oxidation in controlling VOC discharge. Catalyst impregnated on activated carbon can serve as a medium for concentrating VOCs prior to oxidizing them in-situ, without oxidizing the base carbon. If the concentration of the locally adsorbed hydrocarbons can be higher, then the oxidation rate can be promoted. This is a practical method of treating air with very lean VOC concentration. Likewise, the activated carbon, being hydrophobic, is a better support than any hydrophilic material during low-temperature combustion because it can prevent the negative effect of generated water to the activity of the catalyst. Precious metals such as platinum and palladium, and metal oxides such as the oxides of first-row transition metals (Co, Mn and Zn), impregnated to activated carbon and some other hydrophobic materials have been studied for VOC oxidation.

Indeed, the utilization of both the adsorption by activated carbon and catalytic oxidation by metal oxide for VOC destruction can prove to be an economical and suitable alternative technology for developing countries like the Philippines.

ITDI(DOST)-DLSU COLLABORATIVE RESEARCH

Recognizing the use of activated carbon in various environmental applications, the Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) has developed a new technology for activated carbon production. The manufacturing process is different from the conventional method because carbonization and activation are carried out in a single step. ITDI has requested the support of the Environmental Engineering Laboratory of De La Salle University (DLSU) to test their AC for possible utilization in air pollution control. DLSU, on the other hand, has agreed on the collaboration in view of their pursuit to develop effective environmental protection technologies.

Since the ITDI-activated carbon production was essentially different from the conventional method, there is a need to assess its surface characteristics and adsorption property. Thus, a study used an existing Temperature Programmed Desorption (TPD) experimental apparatus with the objective of characterizing the adsorptive capacity of ITDI activated carbons (AC1) by comparing it with a commercial activated carbon (AC2) using three common types of VOCs. These are benzene, toluene and xylene. In particular, it compared the (a) peak temperatures and (b) breakthrough volumes of the ITDI activated carbon with a commercial activated carbon.

Likewise, concentration of the VOCs prior to on-site oxidation is a logical consideration. The use of metal oxides, instead of noble metals, as the active materials impregnated on the activated carbon can be a practical means of oxidizing these organic pollutants. Thus, this part

of the project investigated the catalytic performance of cerium oxide supported on these two activated carbons in the oxidation of a specific VOC, xylene. Optimum CeO_2 loading was also assessed based on the activity of catalysts prepared in different ceria loading.

METHODOLOGY

Figure 1 shows the schematic diagram of the TPD experimental set-up. It consists of a saturator, four-way valve, reactor, furnace, type K thermocouple, thermal conductivity detector (TCD), temperature programmable controller, six-way valve, sampling column, flow meters, Gas Chromatograph and recorder.

Helium is used as a carrier gas for the saturator and the TCD. A saturator is installed for the vaporization of liquid VOCs. The carrier gas is dispersed as a stream of bubbles in the liquid VOC solutes through a fritted tube disperser. The carrier gas along with the vaporized VOC, pass through the mainline pipe and are collected in the sampling column of the six-way valve. The six-way valve is responsible for carrying out gas adsorption by pulse injection. The gas mixture directed to the reactor by pulse injection is equal to the volume of the sampling column.

For the activity tests conducted on different catalysts prepare, a flow reactor system equipped with a Gas Chromatography apparatus was used. Figure 2 shows the schematic diagram of the set-up. Oxygen is used for combustion to occur. The flowrates of oxygen and the VOC-saturated helium are measured and kept constant using the attached rotameters.

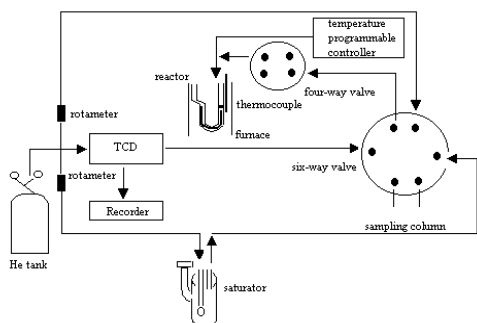


Fig. 1 – TPD Experimental Set-up

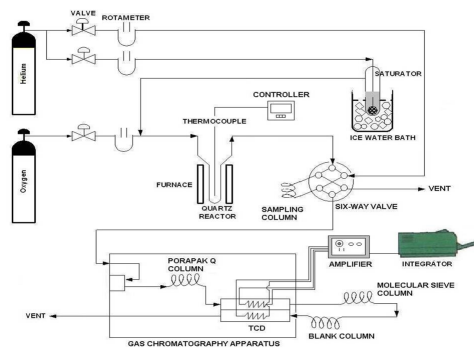


Fig. 2 – Flow Reactor Set-up

DISCUSSION OF RESULTS

Figure 3 shows the relationship between the heating rate and the peak temperature. Generally, it can be observed that as the heating rate is increased, peak temperature also increases. An adsorbate with a higher boiling point will be adsorbed more strongly than an adsorbate with a lower boiling point. Thus, it is expected that xylene has the highest peak temperature as it has the highest boiling point among the three VOCs tested.

In Figure 4, the calculated breakthrough volumes of the two activated carbons for benzene, toluene and xylene are plotted. The breakthrough volumes expressed in L/g activated carbon are 0.1832 for benzene-AC1, 0.6595 for benzene-AC2, 0.0691 for toluene-AC1, 0.2721 for toluene-AC2, 0.0400 for xylene-AC1 and 0.0647 for xylene-AC2. It can be observed that the breakthrough volume of benzene is greater than that of toluene and xylene. Also, the adsorption capacity of AC2 is four times that of AC1. This was confirmed by BET surface area measurement. The surface areas of AC1 and AC2 are 195.58m²/g and 805.15m²/g respectively.

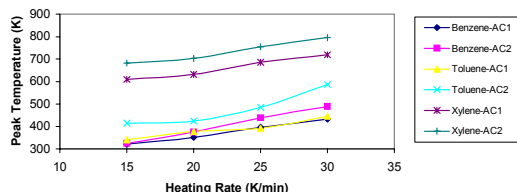


Fig. 3 – Peak Temperatures vs Heating Rate

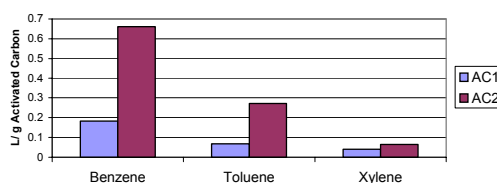


Fig. 4 – Breakthrough Volumes of ACs

The ignition temperature of each activated carbon, AC1 and AC2 was determined by passing oxygen over the AC. Ignition starts when CO₂ begins to be formed and O₂ is consumed. The ignition temperature of AC2 is approximately 300°C. Meanwhile, AC1 begins to ignite at about 250°C. Thus, oxidation reaction was carried out 50°C below their maximum temperature.

The two activated carbons, AC1 and AC2, were both used as support material for cerium oxide. The catalysts, CeO₂/AC1 and CeO₂/AC2, were prepared at 5% ceria loading by the incipient wetness method of impregnation. This uses cerium nitrate salt dissolved in water and small amount of methanol to penetrate the pores of the activated carbon. The time course activity of the catalysts at 200°C is shown in Figures 5 and 6 for CeO₂/AC1 and CeO₂/AC2 respectively. Ceria supported on AC2 has higher activity than ceria supported on AC1. This activity is in terms of xylene conversion and yield of CO₂. Both catalysts show one hundred percent selectivity to CO₂ over CO. The higher activity of ceria supported on AC2 is mainly due to the higher surface area AC2 has than AC1.

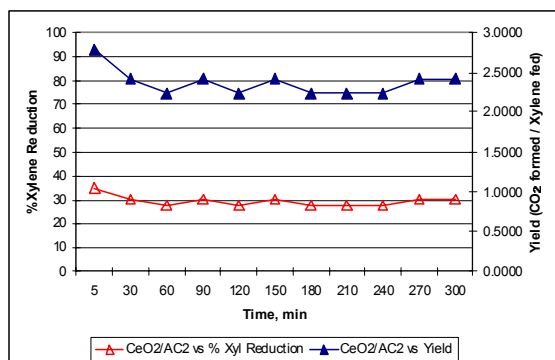


Fig. 5- Time Course Activity for CeO₂/AC1

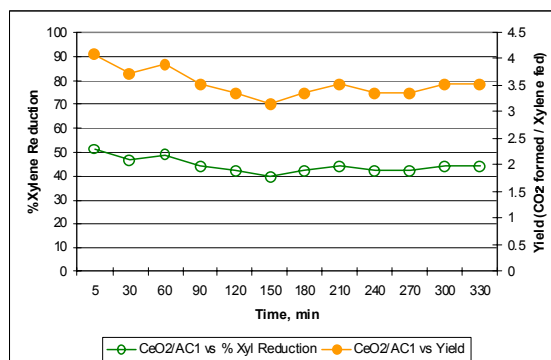


Fig. 6- Time Course Activity for CeO₂/AC2

Figures 7 and 8 show the effect of temperature on the activity of the two catalysts prepared. It can be shown that although no CO_2 is formed at 50° and 100°C , xylene conversion takes place. This is indicative of adsorption of xylene taking place at low temperatures. At higher temperatures, xylene is desorbed and the metal oxide becomes active. Thus, xylene oxidation takes place and CO_2 is formed. Ceria is shown to be an active metal oxide for xylene oxidation since selectivity to CO_2 is 100% at all temperatures higher than 100°C .

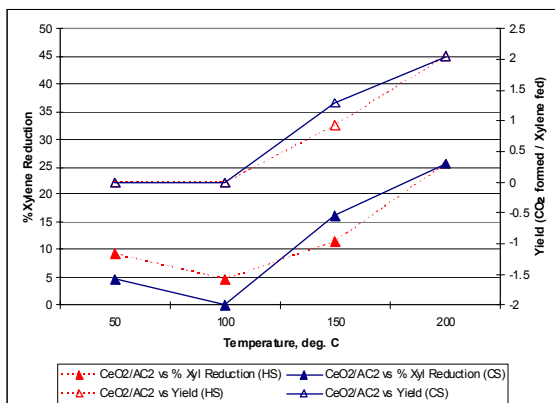


Fig. 7 – Effect of Temperature on Activity of $\text{CeO}_2/\text{AC1}$

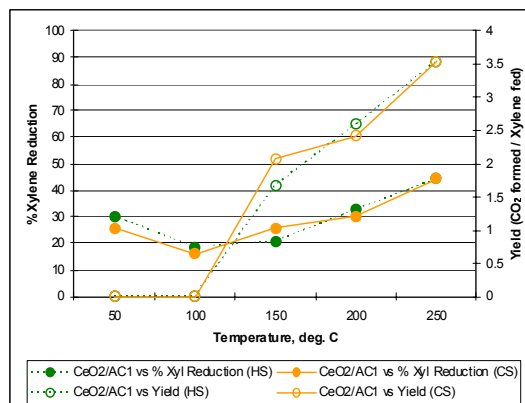


Fig. 8 – Effect of Temperature on Activity of $\text{CeO}_2/\text{AC2}$

Lastly, the effect of varying the ceria loading was also investigated. In Figure 9, the higher the ceria loading, the xylene reduction increases at 200°C . However, in terms of CO_2 yield, the 15% ceria loading gave the highest value.

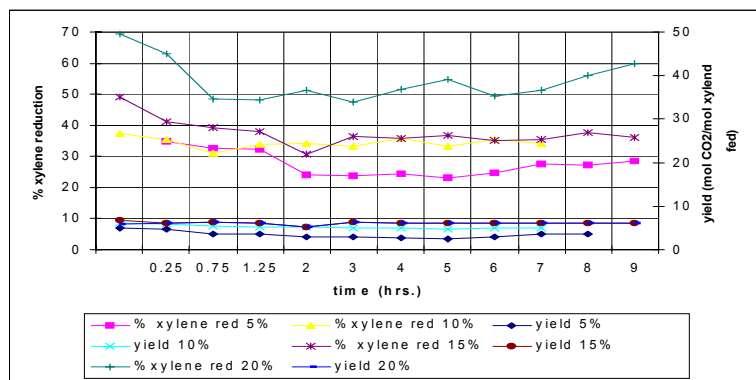


Fig. 9 – Time Course Activity of $\text{CeO}_2/\text{AC2}$ Catalysts at 200°C

CONCLUDING REMARKS

Adsorption-catalytic oxidation is an alternative technology for the treatment of VOCs. The use of activated carbon for this purpose has been elucidated. ITDI activated carbon (AC1) has been proven a good adsorbent for VOCs like benzene, toluene and xylene but the commercial one (AC2) is much better. It is also a promising support material for oxidation catalyst used primarily at low temperatures not exceeding its ignition temperature. ITDI activated carbon (AC1) has lower ignition temperature than that of the commercial one

(AC2). At the same time, the surface area of AC2 is four times the surface area of AC1. TPD has proven that the adsorption capacity of AC2 is also four times that of AC1. Further improvement of AC1 is currently being studied by thermal treatment and acid washing.

Cerium oxide or ceria has proven to be a moderately active oxidation catalyst for xylene at low temperatures like 200°C. Although its temperature can be increased for higher activity, the reaction temperature is limited by the presence of activated carbon support material. Optimum ceria loading is 15% on activated carbon; however, more active metal oxides at low temperature may be investigated in the future.

ACKNOWLEDGEMENTS

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.One available method of evaluating these properties is through the use of temperature-programmed desorption (TPD) technique. This method is very useful in studying surface reactions and molecular adsorption in surfaces.

Aside from VOC recovery by adsorption, other destruction technologies are available and some are still being developed or improved. This is due to more stringent regulations to improve air quality. Destruction devices entail the thermal or catalytic oxidation of these air-polluting compounds to harmless carbon dioxide and water (Chu & Windawi, 1996). Between the two types of VOC oxidation process, the catalytic oxidation proves to be more advantageous than the thermal combustion process. This is because VOC oxidation over a catalyst proceeds faster, and allows a lower operating temperature for the same amount of conversion with that in the thermal process. This translates to improved economics for fuel consumption and reduced expenses for reactor construction materials, since corrosion is minimized (Wu & Chang, 1998; Heck & Ferrauto, 1995; Chu & Windawi, 1996).

Catalytic materials employed in the oxidation of VOCs are generally the base metal oxides (e.g. Cr_2O_3), precious metals (e.g. Pt and Pd) and combinations of both (Heck & Ferrauto, 1995). Supported noble metals, especially Pt and/or Pd dispersed on carriers, are known to dominate the VOC oxidation catalysts with their high activity; good poison resistance, ability to be regenerated, and thermal durability (Shelley, 1997; Heck & Ferrauto, 1995; Chu & Windawi, 1996). However, these catalytic materials, because of their rarity, high demand for environmental and industrial applications, and thus, expensiveness, may prove to be unsuitable to developing countries like the Philippines. Nevertheless, studies (Drago, et al., 1995; Nwankwo & Turk, 1975; Gallardo, Aida & Niiyama, 1998; Vandersall, et al., 1994) have investigated and proven the good catalytic performance of possible alternatives to noble metals – supported metal oxides – in oxidizing harmful organics. One of the metal oxides utilized for oxidation is alumina-supported ceria, which has been proven in a study conducted by the DLSU's Environmental Engineering Laboratory (Gallardo, et al., 1998) to be a promising oxidation catalyst of hydrocarbons, as well as carbon monoxide, from automobile exhaust emissions.

On the other hand, several studies, (Nwankwo & Turk, 1975; Drago, et al., 1995; Wu & Chang, 1998; Kullavanijaya, Trimm & Cant, 2001) have demonstrated the benefits of combining the processes of adsorption (using activated carbon or other adsorbents), and catalytic oxidation in controlling VOC discharge. Catalyst impregnated activated carbon can serve as a medium for concentrating VOCs prior to oxidizing them in-situ, without oxidizing the base carbon. If the concentration of the locally adsorbed hydrocarbons can be higher, then the oxidation rate can be promoted. (Nwankwo & Turk, 1975). This is a practical method of treating air with very lean VOC concentration. Likewise, the activated carbon, being hydrophobic, is a better support than any hydrophilic material during low-temperature combustion because it can prevent the negative effect of generated water to the activity of the catalyst (Wu & Chang, 1998). Precious metals such as platinum and palladium, and metal

oxides such as the oxides of first-row transition metals (Co, Mn and Zn), impregnated to activated carbon and some other hydrophobic materials have been studied for VOC oxidation.

The results of the research projects earlier described in Chapter 1 and Chapter 2 led to the development of more useful application of activated carbon in catalytic oxidation of small concentration of VOC in air. Indeed, the utilization of both the adsorption by activated carbon and catalytic oxidation for controlling VOC emissions can prove to be an economical and suitable alternative for developing countries like the Philippines.

In this project, concentration of the VOCs prior to on-site oxidation is a logical consideration. Likewise, the use of metal oxides, instead of noble metals, as the active materials impregnated to the activated carbon can be a practical means of oxidizing organic pollutants.