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An investigation of nanostructured vanadia/titania catalysts for the oxidation of monochlorobenzene

John L. Graham [a], Catherine Bothe Almquist [b,*], Sachin Kumar [b], Sukh Sidhu [a]

[a] *Environmental Science and Engineering, University of Dayton, Research Institute, Dayton, OH 45469, USA*
[b] *Department of Paper Science and Engineering, Miami University, Oxford, OH 45056, USA*

Abstract

In this work, the effects of V/Ti mass ratios in nanostructured V_2O_5/TiO_2 catalysts on catalyst characteristics and catalyst activity were investigated. The destruction of monochlorobenzene was used as a measure of catalyst activity. The V_2O_5/TiO_2 catalysts, which have been traditionally used as de-NO_x catalysts and selective oxidation catalysts (e.g. in the production of phthalic anhydride), were made by the wet incipient method. This synthesis method provides nanostructured V_2O_5/TiO_2 catalysts with the vanadium species on the surface of the TiO_2. The catalysts were characterized using X-ray diffraction (XRD), BET surface area, and Raman spectroscopy.

The performance of the catalysts for the destruction of organic pollutants was assessed in a differential tube flow reactor for gas-phase thermal oxidation reactions. It was found that the presence of crystalline V_2O_5 on the surface of TiO_2 (V/Ti mass ratio 0.05 and 0.1) is necessary for the oxidation of monochlorobenzene at temperatures <300 °C.

Keywords: Vanadia/titania catalysts; Oxidation; Monochlorobenzene; Nanostructured

1. Introduction

The oxidation of organic vapors is an important component of environmental compliance. This is often achieved through some form of thermal process such as controlled high-temperature incineration, fume incineration and regenerative or recuperative thermal oxidation. These processes, while effective, require very high-temperatures, usually on the order of 800–1000 °C. Maintaining the necessary harsh conditions may require the consumption of large amounts of fossil fuels and may also lead to the formation of undesirable end products such as oxides of nitrogen or even hazardous organic compounds. An alternative approach is to utilize catalytic oxidation. Through the proper selection of the catalyst media high efficiency can be obtained at much lower temperatures, conditions in the range of 200–300 °C are typical. At these relatively mild conditions equipment is easier to design and maintain, and capacity is higher. Furthermore, catalysts can offer high selectivity for desirable end products and will not produce oxides of nitrogen under typical operating conditions. A significant challenge of utilizing catalysts for environmental compliance is the high cost of the precious metal catalysts used and their susceptibility to physical and chemical damage. Consequently, there is interest in developing alternative catalysts that are less expensive and more robust than the materials presently in wide use. One strategy to improve the activity of alternative catalysts is to manufacture them as nanostructured materials

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[*] Corresponding author. Tel.: +1-513-529-2203; fax: +1-513-529-2201.
E-mail address: almquic@muohio.edu (C.B. Almquist).

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either in the form of nanoparticles or with nanoscale crystallites.

Vanadia/titania (V_2O_5/TiO_2)-based catalysts are commonly used in selective catalytic reduction (SCR) because of their high catalytic activity and thermal stability [1]. V_2O_5/TiO_2-based catalysts also exhibit resistance against SO_2 poisoning, which is generally present in exhaust gases from stationary combustion sources [2]. V_2O_5/TiO_2 based catalysts have also been recently used to control emissions of chlorinated organics including chlorinated dioxins, furans and benzenes [3–5]. The results of experiments with chlorinated volatile organic compounds (VOCs) such as methylene chloride, dichloromethane, ethyl chloride, dichloroethane, tetrachloroethene, tetrachloromethane, and chlorobenzenes have been reported [3–6]. In these studies, the effective temperature for the destruction of the chlorinated VOCs was found to be above 300 °C. Only the TiO_2-based V_2O_5/WO_3 catalysts showed effective destruction of tetrachloroethene at temperatures less than 300 °C (230 °C). It becomes evident from results of recent studies that V_2O_5/TiO_2-based catalysts with increased oxidation potential due to higher vanadium content can be optimized to control both NO_x and organic pollutant emissions [6]. However, a further increase in catalyst efficiency is needed for V_2O_5/TiO_2-based catalysts before they can meet emissions standards for VOCs. Also there is a need to eliminate formation of higher chlorinated products, which have been observed in previous pollutant oxidation studies [7].

One approach to improving the efficiency of catalytic materials is preparing them as nanoscale particles (mean diameter <100 nm). It has been shown that nanoparticles are often far more reactive than materials in the bulk phase. Hence, it is possible that nanoparticle catalysts of V_2O_5/TiO_2 will be able to reduce NO_x and oxidize organic pollutants with increased efficiencies so as to comply with existing and future environmental emission standards. There is also need to address inconsistencies in the literature regarding the effects of catalyst properties and synthesis methods on V_2O_5/TiO_2 performance. For example, there are controversies in the literature about the role of the TiO_2 crystalline phase in determining the characteristics of the active phase of V_2O_5/TiO_2 catalysts [8], although it is generally stated that anatase TiO_2 is a more active support than rutile TiO_2 [8]. The optimum vanadium content has been reported to be as low as 4% [9] and as high as 30% [10], depending upon the catalyst synthesis method and the reaction conditions. The thermal stability of the V_2O_5/TiO_2 catalysts is dependent upon the catalysts synthesis method and how the selective catalytic reduction (V) species is incorporated into or onto the TiO_2. This has implications on the TiO_2 crystal phase, and ultimately, the stability of the catalyst over time.

The goals of this study were to investigate the effect of V/Ti mass ratio on TiO_2 phase transformation from anatase to rutile, surface area reduction (degree of sintering), and catalyst activity for the oxidation of monochlorobenzene (MCBz). MCBz was selected because it is emitted from many combustion-based manufacturing processes, cement kilns and incinerators. To accomplish our experimental goals, V_2O_5/TiO_2 catalysts were synthesized with a range of V/Ti mass ratios from 0 to 0.1, and for each V/Ti ratio, the catalysts were calcined in air at temperatures from 400 to 600 °C. The catalysts were characterized using X-ray diffraction (XRD), BET surface area, and Raman spectrometry.

2. Experimental

2.1. Catalyst synthesis

The catalysts used in this study were prepared by the wet incipient method. Briefly, 60 ml deionized water was added to 5 g of Degussa P25 TiO_2 (surface area 50 m^2/g, anatase fraction 80%, and anatase crystal size 20 nm [11]) and stirred using a magnetic stirrer. A measured amount of ammonium metavanadate (Fisher Scientific) was added to the slurry to achieve V/Ti mass ratios ranging from 0 to 0.1. The slurry was heated to approximately 70 °C and stirred constantly to evaporate the water until the slurry was a thick paste. This paste was dried in an oven at 103 °C overnight. Once dry, the powder (V_2O_5/TiO_2) was crushed using a mortar and pestle and separated into 1 gm aliquots. The aliquots were calcined at 400, 500, 550 or 600 °C in air for 24 h. After calcination, the powders were crushed again using a mortar and pestle, and transferred to a vial for storage until subsequent characterization.

2.2. Catalyst characterization

2.2.1. X-ray diffraction

The TiO_2 crystal phase of each catalyst was characterized using a Scintag X-ray Powder Diffractometer (XRD) with a Cu Kα source from $20^\circ < 2\theta < 60^\circ$ at a scan rate of 1°/min. The XRD was equipped with voltage and current stabilizers and a computer with necessary software to record the diffraction patterns. It was operated at a voltage of 40 kV with a filament current of 35 mA. The XRD data were used to study the effect of calcination temperature and V/Ti mass ratio on the phase conversion of TiO_2 from anatase to rutile, the latter being less desirable for catalysis [8].

2.2.2. BET surface area

The surface area of each catalyst was measured using nitrogen adsorption at 77 K using a Beckman-Coulter SA3100 surface area analyzer. Prior to analyses, the catalysts were degassed at 120 °C with a helium purge for 60 min.

2.2.3. Raman spectroscopy

Raman spectra were collected using a Renishaw 2000 confocal Raman microprobe. Samples were excited with a HeNe (632 nm) laser. This source was focused onto the sample using a 50× (0.85 N.A.) objective, which produced an approximate beam diameter of two micrometers at the sample. Power at the sample did not exceed 6 mW. The same objective was employed to collect the scattered radiation. Spectra were collected at $4\,cm^{-1}$ resolution and represent the average of five individual scans. The integration time for each spectral element was 30 s. V species peaks that were not observed using XRD were observed in samples with V/Ti mass ratios ≥ 0.05.

2.3. Catalyst performance

The overall activity of each catalyst for the oxidation of monochlorobenzene (Aldrich, 99.99%) was determined using a flow reactor system called the thermal stability analyzer (TSA). Fig. 1 shows the TSA as configured for this study. As this figure shows, the reactor assembly consists of a sample inlet system, a quartz tubular flow reactor, and a total hydrocarbon analyzer. The sample inlet system includes a syringe pump to meter the sample into the inlet stream and a mixing tee. The reactor is a quartz tube in which 20 mg of catalyst is captured between a pair of quartz wool plugs and positioned at the mid-point of a single zone tube furnace. The total hydrocarbon analyzer consists of a helium make-up inlet, a mixing tee, and a hydrogen flame ionization detector (HFID). Note that the HFID is a very sensitive detector that responds linearly to organic vapors and does not respond to inorganic

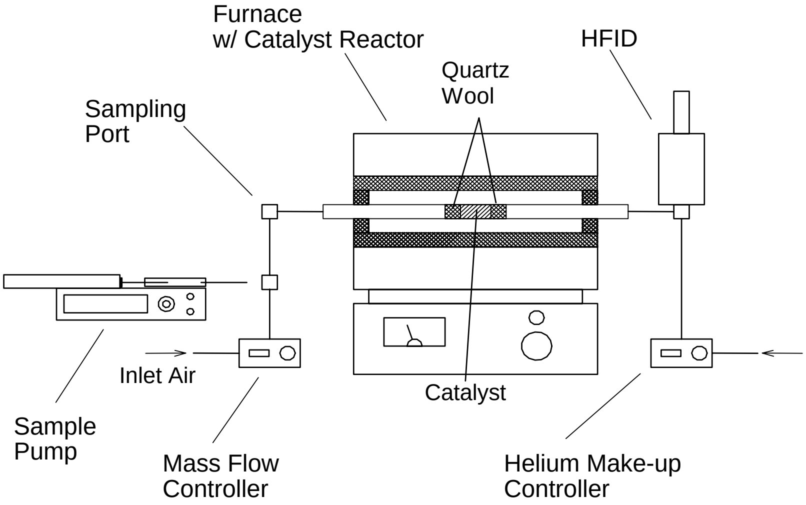

Fig. 1. Schematic of the experimental test system with differential catalytic flow reactor (the thermal stability analyzer) for measuring catalyst activity.

gases. Consequently, the output of this detector is linearly proportional to the concentration of organic species in the reactor effluent. As configured for this study the method detection limit was 0.03 ppmv, which is equivalent to a fraction remaining of 0.01%.

A stock sample of MCBz vapor was prepared by injecting 20 μl of liquid MCBz into a clean glass sample tube filled with 450 ml of dry air drawn from the same compressed gas cylinder used to supply the reactor system and allowed to evaporate. From this stock sample 10 ml was drawn from the sample tube using a gas-tight syringe. A fresh stock sample was prepared for each test.

For each analysis a reactor tube was assembled with approximately 20 mg of catalyst. The catalyst bed was configured using a tight-packed powder design developed previously for measuring the activity of small fixed beds of fine powdered catalysts [12]. Briefly, a tuft of quartz wool is positioned at the midpoint of the reactor tube. The inside face of the tuft was tamped and shaped into a densified flat face. With the reactor tube held vertically the measured catalyst powder was then placed on this prepared face using a long stem glass pipette. An ultrasonic shaker was then applied to the reactor tube to settle the powder into a compact layer lying on the face of the tuft. A matching quartz wool tuft was then inserted into the reactor tube and tamped in place. The catalyst bed was then inspected visually to make sure the bed was in the form of a dense packed layer securely held in place between the two quartz wool tufts. The reactors were also inspected after being removed from the furnace to make sure settling did not occur during the tests. The finished bed measured approximately 2 mm long by 4 mm in diameter. A photograph of the powdered catalyst secured in the reactor is shown in Fig. 2. The prepared reactor tube was then mounted in the tube furnace and the gas connections made. Dry air was then supplied to the reactor with mean flow rate of 64.8 μl/s and the reactor was heated to the temperature at which the catalyst was calcined. The sample was then fed into the reactor inlet at a constant rate of 1.68 μl/s giving a mean initial concentration of 265 ppmv. The combined flow rate of the inlet and sample gases gave a mean residence time at 450 °C of 0.124 s, or a mean space velocity of 29,000 h^{-1}. Once the total hydrocarbon analyzer indicated the reactor was at steady-state (i.e. the HFID output and system temperatures were stable for 10 min) the reactor was cooled at approximately 2 °C/min.

The raw data from the total hydrocarbon analyzer was in the form of the HFID signal and temperature recorded at 1 s intervals. The HFID signal was converted to fraction remaining by first subtracting the baseline signal recorded prior to feeding the sample to the reactor, then normalizing by the average steady-state signal recorded at the end of the run.

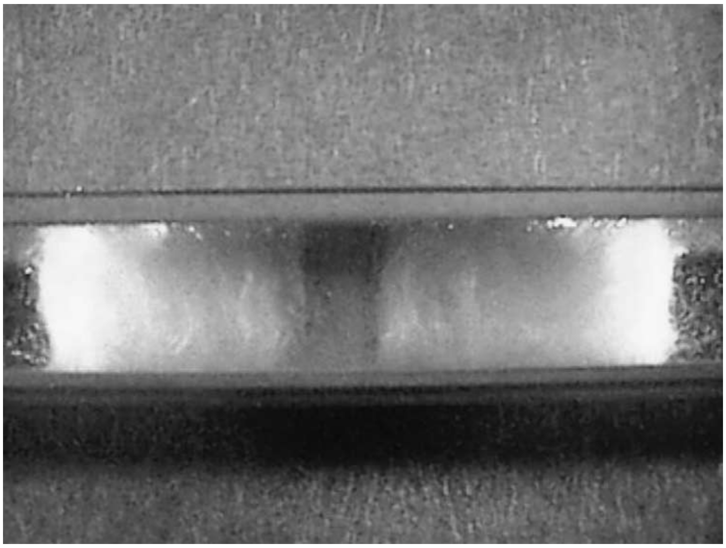

Fig. 2. Photograph of the fine powder catalyst secured in quartz reactor tube. Dimensions of catalyst plug are 2 mm × 4 mm in diameter.

3. Results and discussion

3.1. Catalyst characterization

The anatase TiO_2 fraction in each prepared catalyst was determined using XRD spectra. The phase conversion as a function of calcination temperature for V-free TiO_2 is shown in Fig. 3. Without the addition of V, the crystal phase of Degussa TiO_2 converts from anatase to rutile at temperatures between 500 and 600 °C.

The anatase fraction of TiO_2 for each sample prepared by the wet-incipient method was calculated using XRD spectra and the equation by Spurr and Myers [13]:

$$f = \frac{1}{1 + 1.265(I_R/I_A)}$$

where f is the fraction anatase, I_R is the intensity of predominant rutile peak ($2\theta = 27.4$), and I_A is the intensity of predominant anatase peak ($2\theta = 25.3$). Fig. 4 shows the anatase fraction in the V_2O_5/TiO_2 catalysts as functions of both the V/Ti mass ratio and calcination temperature. The V/Ti mass ratio at calcination temperatures up to 500 °C had little effect on the anatase fraction present in the catalysts. At calcination temperatures of 550 and 600 °C, the presence of low concentrations of V (V/Ti mass ratio $\leq$ 0.02) inhibited the phase transformation of anatase to rutile TiO_2, whereas at V/Ti mass ratios of 0.05 and 0.1, the V appeared to promote the anatase to rutile phase transformation. This is suggested by the maxima anatase fraction at a V/Ti mass ratio of 0.02 in the 550 and 600 °C calcination temperature plots (Fig. 4). These results support the conclusion presented by Balikdjian et al. [14] that a minimal amount of surface V species is required to decrease the temperature at which phase transformation occurs.

Fig. 5 shows the reduction in BET surface area as functions of calcination temperature and V/Ti mass ratio. As shown, there is little effect of V/Ti mass ratio on BET surface area reduction at V/Ti mass ratios up to 0.02, suggesting that the catalysts with low amounts of V species on the surface sinter to the same extent as catalysts without V. However, at V/Ti mass ratios of 0.05 and 0.1, the BET surface area reduction, or degree of sintering, increases with increasing V/Ti mass ratio. Besselmann et al. [15] observed that the V species on the surface of V_2O_5/TiO_2 catalysts when present in low concentrations are predominantly monomeric and polymeric species in strong interaction with the TiO_2 support. At high V concentrations, the V species on the surface of the catalysts are predominantly polymeric and crystalline vanadia species. Considering the BET surface area, XRD, and Raman (next section) data for our catalysts, and the observations by Besselmann et al. [15], monomeric and polymeric

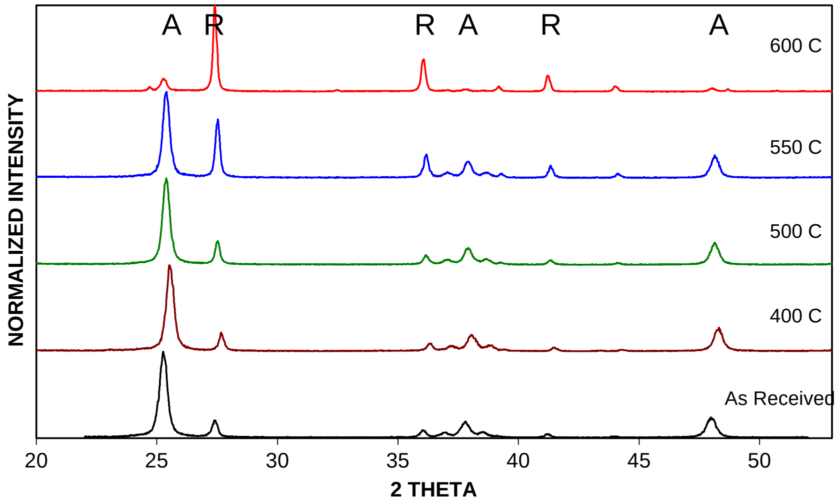

Fig. 3. X-ray Diffraction spectra for Degussa P25 as received and after calcination in air for 24 h at temperatures of 400, 500, 550, and 600 °C. A: anataseTiO_2; R: rutile TiO_2.

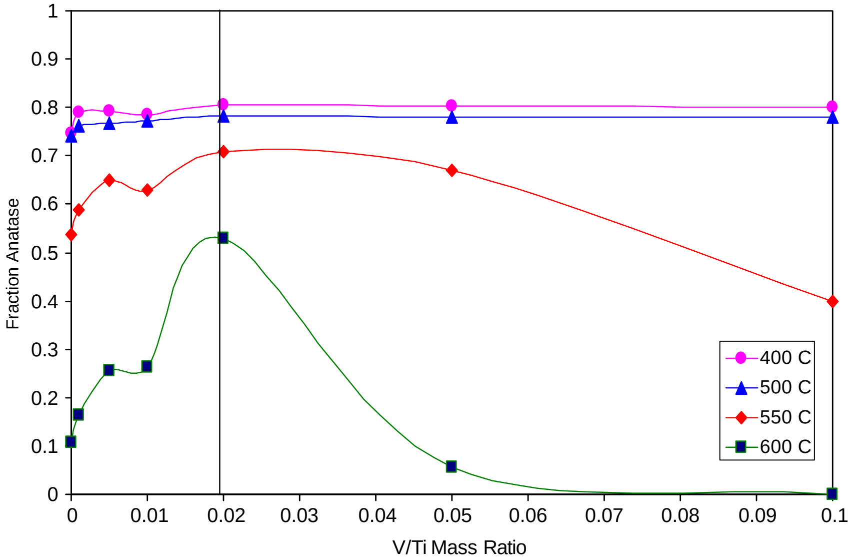

Fig. 4. Fraction anatase TiO_2 in V_2O_5/TiO_2 catalysts as functions of V/Ti mass ratio and calcination temperature.

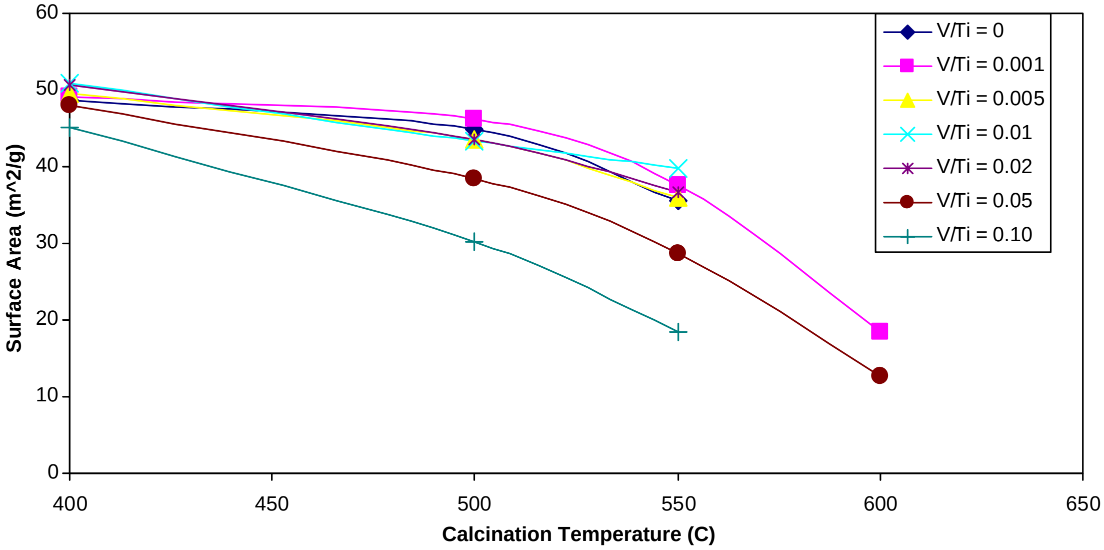

Fig. 5. BET surface area reduction as functions of calcination temperature and V/Ti mass ratio.

species in strong interaction with the TiO_2 may indeed inhibit phase transformation, whereas crystalline and polymeric vanadia at the surface of the catalysts (present in our catalysts with V/Ti mass ratios of 0.05 and 0.1) promote sintering and anatase to rutile phase transformation.

Fig. 6 shows a summary of Raman spectra of V_2O_5/TiO_2 catalysts calcined at 400 °C. V peaks were observed in catalysts with V/Ti mass ratios of 0.05 and 0.1 at approximately 995 cm^{-1}, which are indicative of terminal V=O groups of bulk V_2O_5 [15]. No other peaks between 900 and 1100 cm^{-1} were

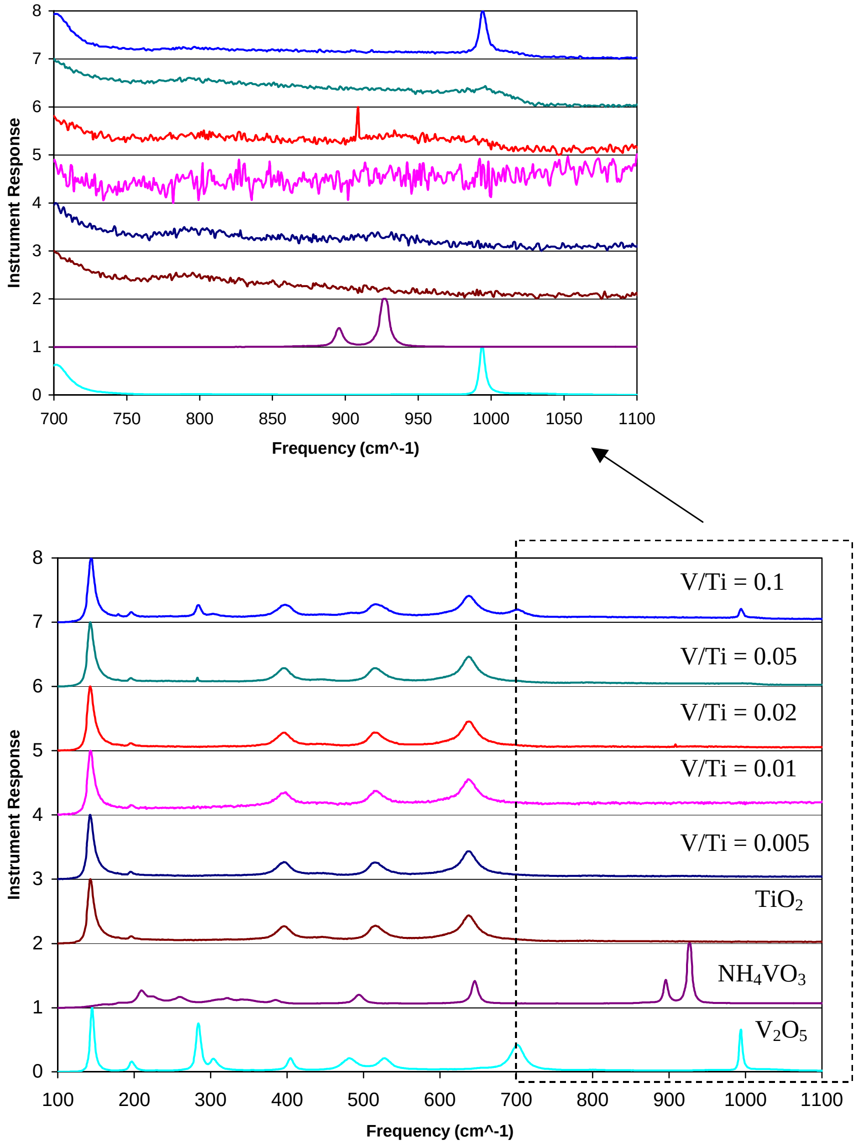

Fig. 6. Raman spectra of catalysts calcined in air at 400 °C for 24 h at varying V/Ti mass ratios.

observed. Because these groups are observed only when the V/Ti mass ratio is 0.05 and 0.1, and because the enhanced degree of sintering and phase transformation is also observed when the V/Ti mass ratio is 0.05 and 0.1, this supports our previous conclusion and that of Besselmann et al. [15] that crystalline vanadia groups on the surface of the TiO_2 are responsible for the enhanced degree of sintering and phase transformation.

3.2. *Catalyst performance*

Catalyst performance was investigated only with catalysts that were calcined at 400 and 500 °C. The selection of these catalysts isolated the effects of V loading on the performance of the catalysts, since the fraction anatase in these catalysts were similar and changes in surface area were relatively small. The results for the destruction of MCBz over the V_2O_5/TiO_2

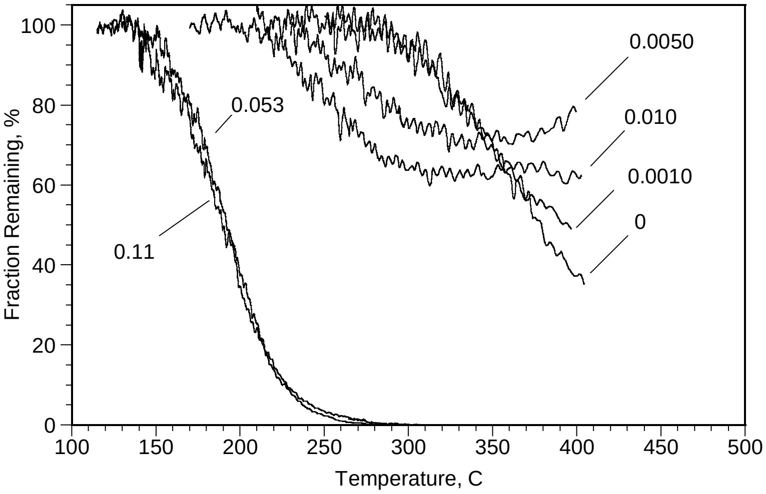

Fig. 7. MCBz degradation in the differential catalytic flow reactor for catalysts calcined in air at 400 °C for 24 h.

catalysts calcined at 400 and 500 °C are shown in Figs. 7 and 8, respectively.

The results presented in Figs. 7 and 8 for catalysts containing V/Ti ratios of 0 and 0.001 show that MCBz is stable in the presence of the catalysts at temperatures up to 300 °C. At temperatures greater than 300 °C, MCBz, or more specifically, the total hydrocarbon content in the reactor effluent, degrades, as indicated by the linear decrease in HFID response with temperature. The decrease in HFID response indicates that MCBz is degraded to inorganic by-products. Although we did not specifically identify the inorganic by-products of MCBz in this study, they are likely to be CO, CO_2, H_2O, and HCl, since the tests were conducted under oxidative conditions.

The results for the catalysts with V/Ti ratios of 0.005 and 0.01 show bimodal behavior, which is typical of TSA data for which the feed material decomposes to form organic by-products in significant yields. The HFID signal for these two catalysts indicates that

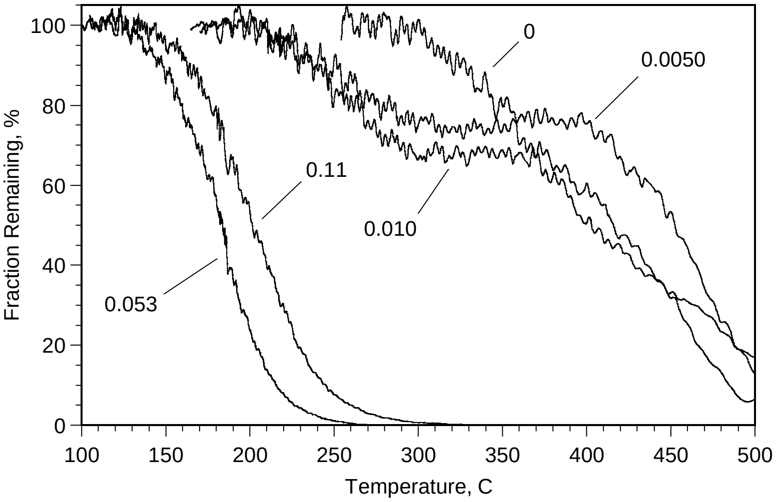

Fig. 8. MCBz degradation in the differential catalytic flow reactor for catalysts calcined in air at 500 °C for 24 h.

MCBz is stable up to 200 °C. The decrease in HFID signal for these catalysts at temperatures between 200 and 300 °C indicates that MCBz starts to degrade to either organic by-products that do not desorb readily from the catalyst or to a combination of organic and inorganic by-products. The stabilized HFID signal observed between 300 °C and approximately 400 °C suggests that MCBz degrades to form organic by-products that are stable in the presence of the catalysts in this range of temperatures. Finally, the decrease in HFID signal at temperatures above 400 °C indicates further degradation of MCBz and its by-products to inorganic compounds that are not detected by the HFID.

The results for the catalysts with V/Ti mass ratios of 0.05 and 0.1 show higher activity than those studied with lower V/Ti mass ratios. The constant decrease in the HFID response at temperatures greater than 150 °C shows effective degradation of MCBz and the organic by-products of MCBz oxidation to inorganic compounds that are not detected by the HFID.

In comparing Figs. 7 and 8, the data also show that the calcining temperature between 400 and 500 °C had very little effect on catalyst performance. Similar trends (fraction remaining versus reaction temperature) were observed for all the catalysts at calcining temperatures, 400 and 500 °C. The reason for the apparently different activity of the catalysts with V/Ti mass ratios of 0.05 and 0.1 when calcined at 500 °C is due to their difference in surface area. At 400 °C calcining temperature, the difference in surface area between the catalysts with V/Ti mass ratios of 0.05 and 0.1 was small (48 m^2/g versus 45 m^2/g); this difference was much more prominent when the catalysts were calcined at 500 °C (38 m^2/g versus 30 m^2/g).

Fig. 9 shows the temperature at which 10% conversion of MCBz is achieved (90% remaining) as a function of V/Ti mass ratio for catalysts calcined at 400 and 500 °C. The results show that the overall catalyst activity increased with V/Ti mass ratios from 0.00 to 0.05. The activities of the catalysts with V/Ti mass ratios of 0.05 and 0.1 were similar.

Only those catalysts with V/Ti mass ratios of 0.05 and 0.1 achieved oxidation of MCBz and the organic by-products of MCBz oxidation at temperatures <250 °C. The TSA data show that organic by-products of MCBz are formed as the V/Ti mass ratio increases up to 0.01, but these by-products oxidize further when the V/Ti mass ratio is increased to 0.05 and 0.1 (Figs. 7 and 8). This behavior clearly suggests a significant increase in catalyst activity for MCBz oxidation as the V/Ti mass ratio is increased to 0.05 and 0.1.

According to Besselmann et al., crystalline and polymeric vanadia at the surface of the catalysts,

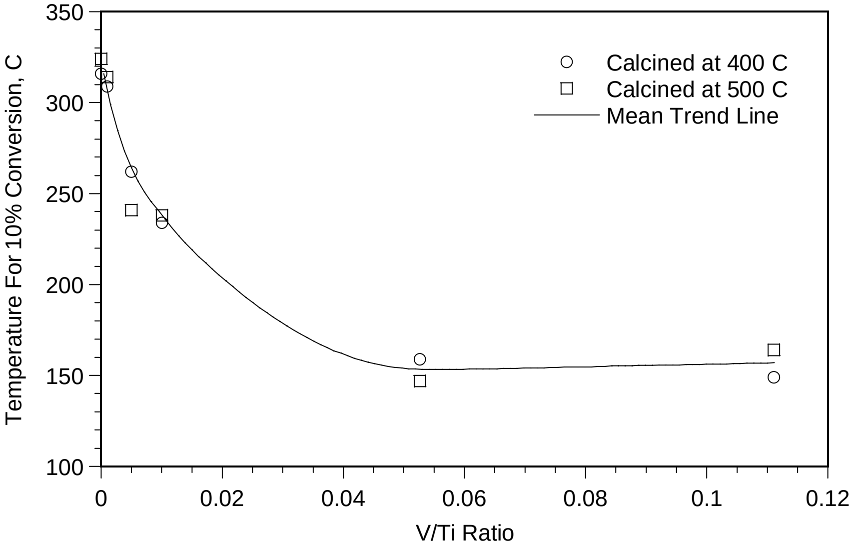

Fig. 9. The temperature for 10% conversion as a function of V/Ti mass ratio and calcination temperature (°C).

which were observed by Raman spectroscopy in our catalysts with a V/Ti mass ratio ≥ 0.05, are able to adsorb gas-phase oxygen and insert it readily into the adsorbed organic species [15]. Contrarily, the monomeric vanadyl species, assumed to be predominant on our catalysts with V/Ti mass ratios < 0.05, function mainly as oxidative adsorption sites for aromatic hydrocarbons [15]. Hence, we observed oxidation of MCBz and by-products of MCBz oxidation at temperatures <250 °C when crystalline and polymeric vanadia sites predominate on the surface. Stable organic by-products of MCBz oxidation were observed at temperatures <400 °C when monomeric V species predominate on the catalyst surface. With trace or no V species on the surface of TiO_2, oxidation of MCBz and its by-products was observed at temperatures >300 °C.

4. Conclusions

This investigation shows that V_2O_5/TiO_2 catalysts can be used to achieve the oxidation of MCBz at moderate temperatures (<300 °C). The data also show that there is a significant increase in the overall activity for MCBz oxidation as the V/Ti mass ratio increased to 0.05. In addition, our data support that crystalline vanadia species on the surface of the catalyst are responsible for higher catalytic activity for the oxidation of MCBz. Calcining temperatures between 400 and 500 °C had only a small effect on the catalyst activity. Future work with this system should include a detailed analysis of the reaction products and kinetics.

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