JOURNAL OF CATALYSIS **162,** 284–294 (1996)
ARTICLE NO. 0286

Oxidation of o-Xylene to Phthalic Anhydride over V_2O_5/TiO_2 Catalysts

III. Study of Organic Residue Formed on the Catalyst Surface

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Received May 24, 1995; revised February 12, 1996; accepted April 30, 1996

An organic residue is formed on V_2O_5/TiO_2 (anatase) catalysts during the oxidation of o-xylene and o-tolualdehyde. V_2O_5 catalysts supported on TiO_2 (0.6, 1, and 5% V_2O_5/TiO_2), prepared by wet impregnation, were exposed to o-xylene/air and o-tolualdehyde/air mixtures under different operating conditions, and, after different times of exposure to reaction conditions, the catalysts were characterized by FTIR spectroscopy and temperature programmed oxidation. The compounds formed were also extracted and analyzed by mass spectrometry. Organic molecules containing no more than two aromatic rings, formed by dimerization of adsorbed molecules, were detected and their characteristics were found to vary with features of the catalytic surface and with operating conditions. Larger contents of residue were obtained at lower temperatures and lower contact times and, for some experimental conditions, a constant amount of such compounds was observed after 1 h of exposure under reaction conditions. The analysis of samples used with different reactant mixtures showed that adsorbed o-xylene can lead to the formation of a "residue" on the surface.

INTRODUCTION

The catalytic oxidation of o-xylene is the most important industrial process for phthalic anhydride production (1, 2). For this reaction, V_2O_5 supported on TiO_2 (anatase) was found to lead to higher activity and higher phthalic anhydride selectivity, when compared with other catalysts (3–10). The main reaction products are phthalic anhydride, o-tolualdehyde, phthalide, and CO_2, but other side products, such as maleic and dimethyl maleic anhydride, o-toluic acid, and CO, can also be detected in very low concentrations (2, 11–16).

Reactions of organic compounds on solid catalysts are sometimes accompanied by the formation of by-products, which can adsorb on the surface and lead to deactivation. For o-xylene oxidation, formation of such compounds has been detected at lower conversions (3, 11, 16, 17), but little information can be found about the characteristics of these compounds and the processes involved in their formation. Wainwright and Hoffman (3) refer to the formation of large amounts of tar using V_2O_5 catalysts supported on silica, but these by-products were neither quantified nor were their characteristics studied. Bond and König (11), studying catalysts prepared by reaction between the hydroxyl groups on the anatase surface and vapor of $VOCl_3$, found that, below 600 K, not all the o-xylene fed to the reactor was recovered as volatile products. The carbon deficit was denoted by a residual selectivity (S_R), which attained values of about 40% at 20% conversion. According to these authors, for o-xylene oxidation, the first reaction step is the adsorption of the organic reactant over HO–V=O sites with formation of species that, on a highly reduced surface, could form strongly adsorbed molecules only removable by nonselective oxidation. Saleh and Wachs (16) studying catalysts prepared by wet impregnation, using a 1.25 mol% o-xylene/air mixture, in the 593–643 K range, obtained, at low conversion (about 5%), tar selectivities of 20%, which were found to decrease for increasing conversions. More recently, Kopinke *et al.* (17) analyzed by mass spectrometry the reaction products of o-xylene oxidation over V_2O_5/TiO_2 catalysts, obtaining information about the oxidation of the organic residue formed. Results showed that the combustion of these products is a catalyzed reaction involving reactive surface oxygen species. Bal'zhinimaev and Pinaeva (18), employing relaxation (nonstationary) methods, studied the reaction mechanism over vanadium–titanium catalysts, concluding that besides the selective and total oxidation products there is also formation of coke-like deposits. Experimental evidence showed that the oxidation of these adsorbed compounds is one important route of formation of CO_2 (18). The formation of such by-products has also been associated with catalyst deactivation (19–21). In fact, the study of the transient regime of o-xylene oxidation over V_2O_5/TiO_2 catalysts showed that a larger decrease of conversion can be connected with a higher residual selectivity (21). Despite all these studies, o-xylene oxidation has been mainly investigated at higher temperatures, with no

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0021-9517/96 $18.00

information about the formation of these undesirable compounds being available.

In the first two parts of these series, we have reported detailed analyses of the products of o-xylene oxidation under transient (21) and steady (22) conditions; a major observation has been that, at low temperatures and low conversions, a considerable fraction of the o-xylene fed to the reactor does not appear as gaseous products, but forms a *residue* of low volatility. The purpose of this paper is to investigate its chemical composition and the mechanism of its formation; the relevance of this study to the problem of designing catalysts that are more selective at high conversion lies in the belief that a major source of carbon oxides may in fact be the same species that constitute the residue at low conversion. Thus, samples of catalysts (0.6, 1, and 5% V_2O_5/TiO_2), prepared by wet impregnation, were exposed to feed mixtures and experimental conditions that favor the formation of an adsorbed residue; catalyst samples were then collected and analyzed by FTIR spectroscopy and temperature-programmed oxidation (TPO). Deposits formed on V_2O_5/TiO_2 samples under different operating conditions were also extracted and characterized by mass spectrometry. The present results shed light on the characteristics of the adsorbed organic residue and on the effect of the experimental conditions on their formation.

EXPERIMENTAL

Preparation of Samples

Catalysts containing 0.6, 1, and 5 w/w% V_2O_5 were prepared by wet impregnation employing an aqueous solution of NH_4VO_3 in oxalic acid. The preparation, activation, and characterization procedures have been described elsewhere (22).

The samples were tested in a conventional flow apparatus at atmospheric pressure and using 0.7 mol% o-xylene/air and 0.5 mol% o-tolualdehyde/air mixtures (22). Before each experiment the fresh catalyst was heated from room temperature to 683 K under air flow and kept under these conditions for 1 h. The system was then cooled to the reaction temperature and, after stabilization, the reactant mixture was fed to the system. Temperatures of 533 and 613 K and contact times (W/F) of 1.6×10^{-5} and 2.5×10^{-4} $kg_{cat}\ dm^{-3}\ h$ were used. To remove samples, the o-xylene/air (o-tolualdehyde/air) flow was interrupted and N_2 switched on. The reactor was kept under N_2 flow until it reached room temperature. Samples were collected after 15 min, 1, 2.5, and 4 h of exposure to reaction conditions (time-on-stream).

Characterization of Catalyst Samples

The characterization of fresh catalyst samples, performed by XRD, BET analysis, laser Raman and FTIR spectroscopy, XPS and TPR, has been described elsewhere (22).

Samples were characterized by FTIR spectroscopy and TPO. Infrared spectra were recorded on a Perkin Elmer 1710 Infrared Fourier Transform spectrometer to which a minicomputer was attached. They were placed on the sample holder in the form of a fine powder, and a 2 cm^{-1} resolution was used. Oxidation of the residue was performed in a conventional TPO apparatus using a 40 $cm^3\ min^{-1}$ (STP) flow of a 6 mol% O_2/He mixture and a 5 K min^{-1} heating rate. Samples were placed in a silica reactor between two pieces of silica wool, on top of which some 5% Pd/SiO_2 catalyst (1 part catalyst : 10 parts sample) was placed, ensuring that any CO formed was oxidized to CO_2. The apparatus and complete experimental procedure have been described elsewhere (23).

Extraction of Adsorbed Residue

Samples were dissolved at room temperature in a 40% HF solution (Merck), the organic compounds being extracted with $CHCl_3$. This was added to the HF solution and the mixture was stirred for 15 min. After separation of the two phases, the extraction was repeated three times. After evaporation of part of the chloroform, the solution was analyzed by mass spectroscopy using a EMI MS 902 mass spectrometer. A sample containing a mixture of anthracene and 1% V_2O_5/TiO_2 was also treated and analyzed according to the previous procedure to check its effect on an aromatic molecule.

RESULTS AND DISCUSSION

The characterization of fresh samples has been reported elsewhere (22). Results showed that the support contained only anatase and that the catalysts containing 0.6, 1, and 5% V_2O_5/TiO_2 had surface areas of 8.7, 7.5, and 6.8 $m^2 g^{-1}$, respectively.

FTIR Studies

The spectra presented in Figs. 1–4 are the difference between the spectra of used and fresh catalysts. Bands can be associated with characteristic organic groups, showing that aromatic molecules are present on the surface. Characteristics of such molecules depended on the operating conditions under which samples had been tested and on the catalytic composition.

Generally, the spectra include a broad O−H stretching band in the region 3600–2900 cm^{-1} (more intense for longer times-on-stream), indicating that the O−H groups interact with other atoms. Free O−H groups, with sharp bands in the 3700–3100 cm^{-1} range, were not detected.

Bands in the 3000–2800 cm^{-1} range can be assigned to the stretching vibration modes of C−H bonds in $>CH_2$ and $-CH_3$ groups. Niwa *et al.* (24), studying the adsorption

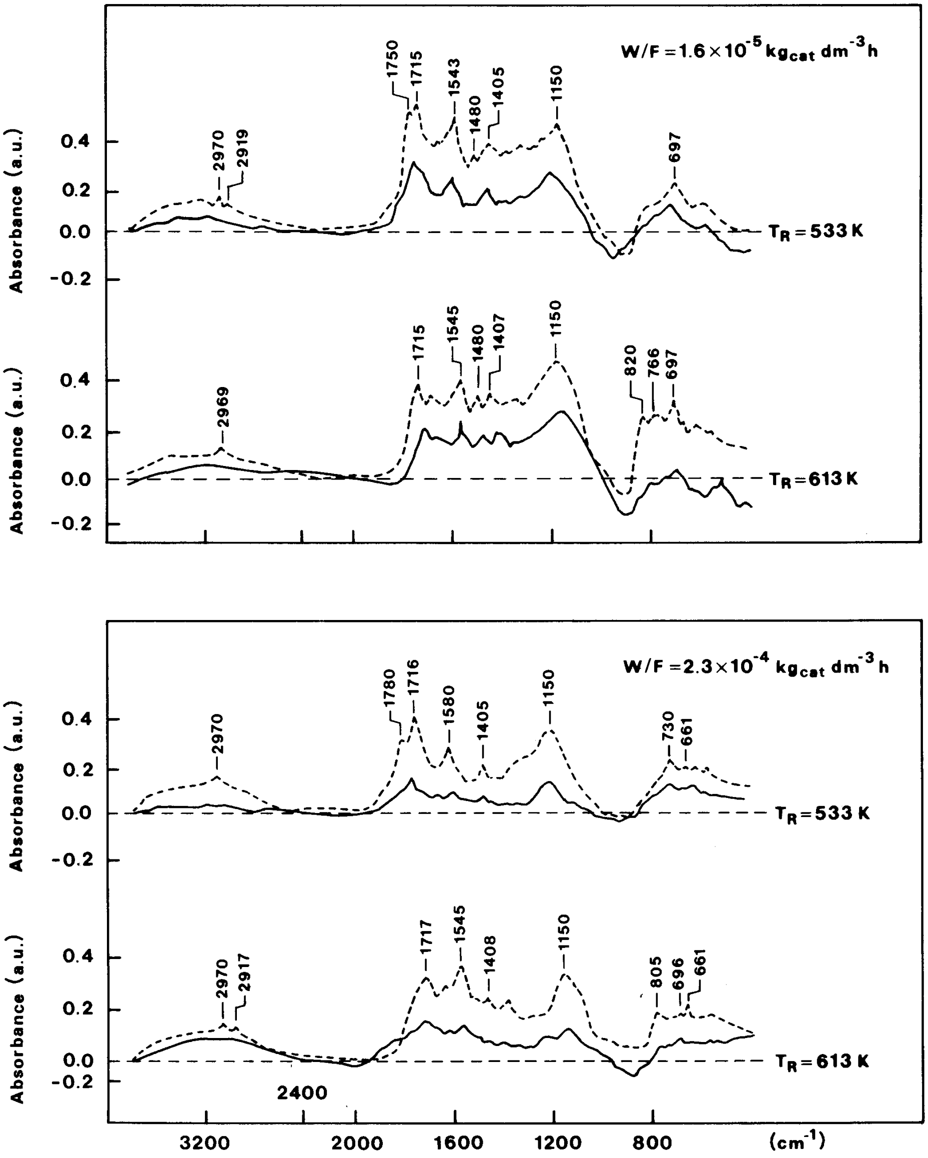


FIG. 1. FTIR spectra of 0.6% V_2O_5/TiO_2 samples tested under o-xylene/air flow, at different temperatures (T_R) and contact times (W/F), after subtraction of the fresh catalyst spectrum. Time of exposure to reaction conditions: ——— 0.25 h; – – – 4 h.

of o-xylene over V_2O_5/Al_2O_3 samples, observed bands at 2975, 2950, and 2930 cm^{-1} (2966 and 2925 cm^{-1} for o-tolualdehyde adsorption), which were found to result from $-CH_3$ groups. For 0.6% V_2O_5/TiO_2 (Fig. 1) these bands appear in the region 2970–2917 cm^{-1}; for 1% V_2O_5/TiO_2 (Fig. 2) bands are detected at 2965, 2938, 2919–2916, and 2907 cm^{-1}, but, for 5% V_2O_5/TiO_2, no important bands are detected in that range (Fig. 3). The samples used for o-tolualdehyde oxidation (Fig. 4) exhibit bands at 2985–2860 cm^{-1}. The spectra show that generally the intensity of bands attributed to C–H bonds increases with time-on-stream.

In the range 1800–1630 cm^{-1}, bands that can be assigned to the stretching of C=O bonds are detected (25, 26). In Figs. 1–4, the presence of carbonyl groups in several species can be observed, the band intensities varying with the time-on-stream. The 0.6% V_2O_5/TiO_2 samples show a band at 1715 cm^{-1} and, at lower temperatures, new bands at 1780 and 1750 cm^{-1} are detected. Spectra obtained with 1% V_2O_5/TiO_2 show several bands in the 1795–1700 cm^{-1} range that may be associated with C=O bond vibrations in different species, that at 1795 cm^{-1} showing decreasing intensity with time-on-stream. At lower W/F, a band at 1715 cm^{-1} emerged as the time-on-stream was increased, the one at 1700 cm^{-1} (detected for samples tested at higher W/F) showing the same behavior. Samples exposed to o-tolualdehyde/air mixtures absorb at 1735 cm^{-1} and 1700–1680 cm^{-1}, whereas for 5% V_2O_5/TiO_2 bands assigned to the

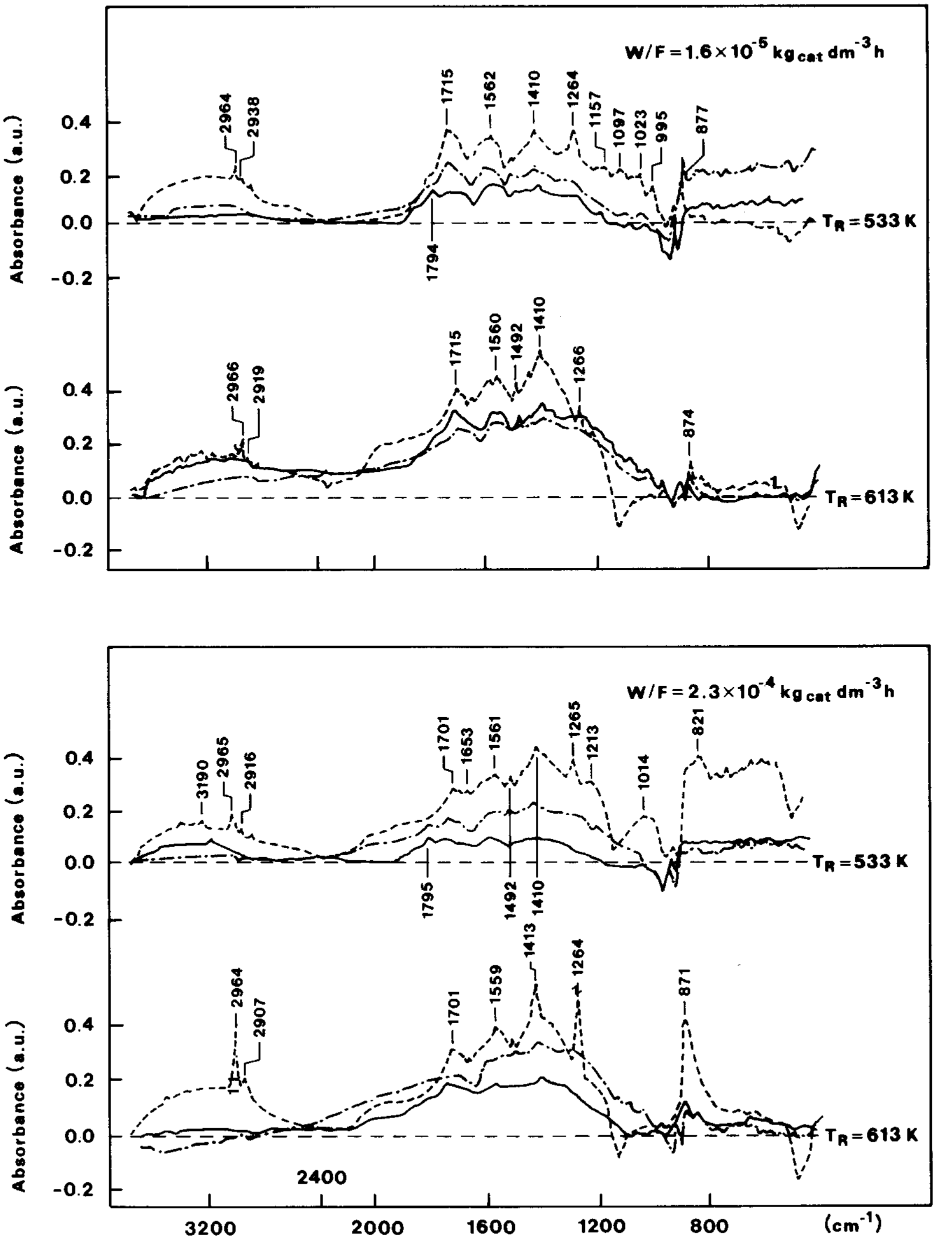


FIG. 2. FTIR spectra of 1% V_2O_5/TiO_2 samples tested under o-xylene/air flow, at different temperatures (T_R) and contact times (W/F), after subtraction of the fresh catalyst spectrum. Time of exposure to reaction conditions: ——— 0.25 h; – · – · 1 h; – – – 4 h.

C=O stretching vibration are detected in the range 1801–1710 cm^{-1}. Bands at 1800 and 1750 cm^{-1}, the last one more intense, are observed at higher W/F, whereas at lower W/F, bands in the regions 1800–1790, 1740, and 1714–1710 cm^{-1}, their intensity depending on the time-on-stream, are observed. The C=O groups detected cannot be assigned to the presence of aldehydes. In fact, the two characteristic bands of this group in the range 2850–2700 cm^{-1}, which can be ascribed to the C–H bond stretching vibration in –CHO groups, were not detected.

Bands in the range 1625–1450 cm^{-1} correspond to the stretching of carbon–carbon bonds in aromatic rings. In fact, studying the adsorption of o-xylene on V_2O_5/TiO_2 samples, van Hengstum *et al.* (27) found bands in the range 1600–1400 cm^{-1} that were attributed to aromatic carbon–carbon bond vibration and, for the adsorption of o-xylene and o-tolualdehyde over V_2O_5/Al_2O_3, Niwa *et al.* (24) observed the same bands at 1600–1450 and 1608–1450 cm^{-1}, respectively. For benzaldehyde adsorption over Al_2O_3, they detected carbon–carbon vibration bands at 1600, 1550, and 1455 cm^{-1}. In Figs. 1–4, bands corresponding to the vibration of carbon–carbon bonds can be observed at 1545–1405, 1562–1410, and 1610–1430 cm^{-1} for 0.6, 1, and 5% V_2O_5/TiO_2 samples, respectively. Generally, these bands

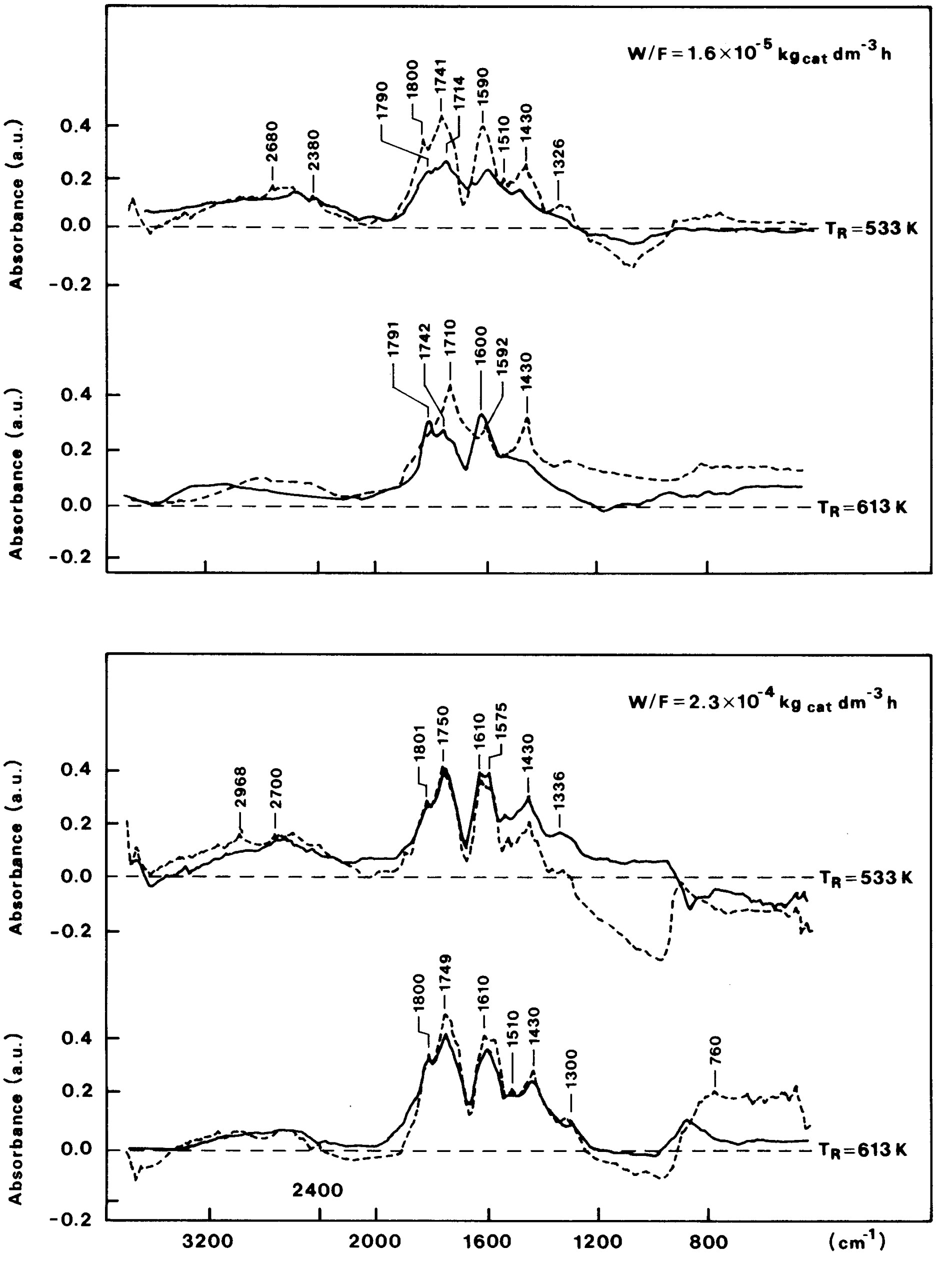


FIG. 3. FTIR spectra of 5% V_2O_5/TiO_2 samples tested under o-xylene/air flow, at different temperatures (T_R) and contact times (W/F), after subtraction of the fresh catalyst spectrum. Time of exposure to reaction conditions: ——— 0.25 h; – – – 4 h.

become stronger as the time-on-stream increases, showing that the time of exposure to reactant mixtures has a large influence on the concentration of adsorbed species. Some bands in this region can also be ascribed to carboxylate groups. van Hengstum *et al.* (27) obtained, for o-tolualdehyde adsorption on V_2O_5/TiO_2, bands at 1500 and 1410 cm^{-1}, which they attributed to the symmetric and asymmetric vibration of adsorbed benzoate species.

Bands ascribed to C–O bond vibration are also detected in the spectra shown in Figs. 1–4. The 0.6% V_2O_5/TiO_2 shows a strong absorption at about 1200 cm^{-1}, whereas for 1% V_2O_5/TiO_2 spectra show an intense band at around 1265 cm^{-1}. For samples tested at 533 K, bands at 1213 and 1014 cm^{-1} (at higher W/F) and 1157, 1097, and 1023 cm^{-1} (at lower W/F) are also detected. The 5% V_2O_5/TiO_2 shows broad weak bands in the 1300–1336 cm^{-1} range and, for o-tolualdehyde oxidation, the spectra contain bands at 1270–1265, 1250, and 1230–1220 cm^{-1}, their intensity increasing with time-on-stream. Bands associated with C–O bonds are stronger at longer times-on-stream.

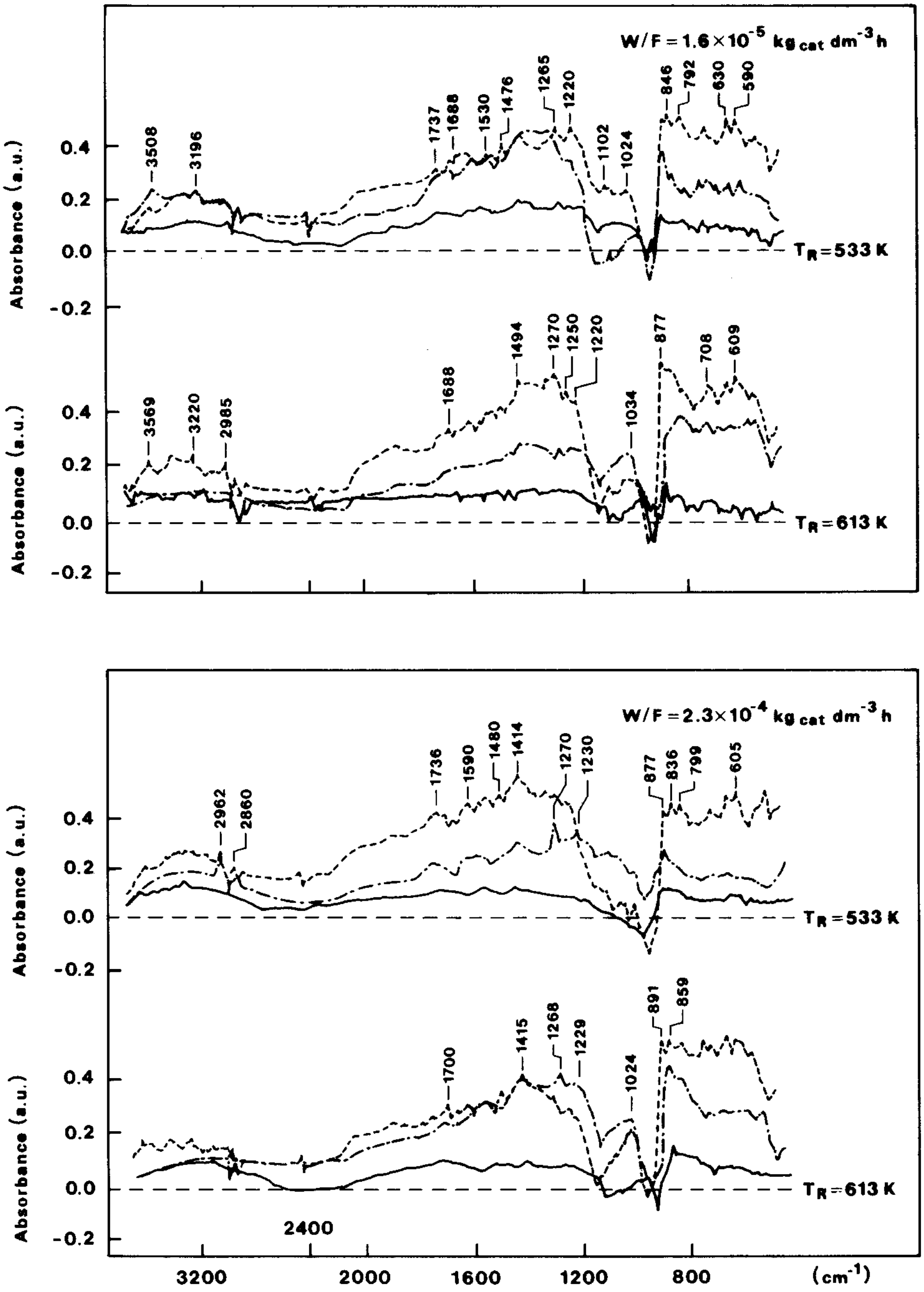


FIG. 4. FTIR spectra of 1% V_2O_5/TiO_2 samples tested under o-tolualdehyde/air flow, at different temperatures (T_R) and contact times (W/F), after subtraction of the fresh catalyst spectrum. Time of exposure to reaction conditions: ——— 0.25 h; – • – • 1 h; – – – 4 h.

Bands in the 900–600 cm^{-1} region correspond to the out-of-plane bending vibration of C–H bonds in aromatic rings, their position being characteristic of the number of adjacent hydrogen atoms in the ring. Bands at 820–661 cm^{-1} are generally observed for the 0.6% V_2O_5/TiO_2 sample, whereas the spectra obtained with 1% V_2O_5/TiO_2, at lower reaction temperature, show bands in the 870–700 cm^{-1} range; in this region, bands corresponding to the stretching vibration of V–O–V structural units at about 820 cm^{-1} are also found (28, 29), and this makes the analysis of spectra difficult.

The subtraction of spectra corresponding to used and fresh catalysts shows that bands in the 1010–870 cm^{-1} range, attributable to the vibration of vanadium–oxygen bonds of surface vanadium species (14, 30–32), are not present in the spectra of used catalysts, implying that such sites have an important role in o-xylene oxidation.

Thus, FTIR spectra show that aromatic molecules are present on the catalysts. They are connected to the surface through lateral groups, bands corresponding to the carbon–carbon aromatic bonds appearing in the usual frequency range. However, for 0.6% V_2O_5/TiO_2 the frequencies of strongest bands in that range (1545, 1480, and 1405 cm^{-1}) are generally lower than those obtained for 1% V_2O_5/TiO_2 (1560, 1492, and 1410 cm^{-1}), showing that, in the former, a stronger interaction between the aromatic ring and the surface could occur. These downward shifts of bands are in agreement with results concerning the adsorption of aromatic rings on oxides where π-bonding was detected (33–35). The characteristics of the adsorbed organic compounds depend on the operating conditions used and on the catalyst composition, carbon–oxygen bonds being highly affected. In fact, new C=O bonds, corresponding to the formation of new surface species, were detected at longer times-on-stream, and bands corresponding to C–O bonds are mainly observed at longer times-on-stream. Also, for 5% V_2O_5/TiO_2, bands corresponding to C=O and C–O appear at higher wavenumber than those for 1% V_2O_5/TiO_2, showing that the presence of higher amounts of crystalline V_2O_5 influences the characteristics of the residue formed.

TPO Studies

Typical TPO plots for used V_2O_5/TiO_2 samples are shown in Fig. 5. These are usually broad peaks containing one or more "shoulders," oxidation of adsorbed compounds starting at 413–513 K and ending in the 643–773 K range. The temperatures corresponding to the maxima of such peaks (T_{max}) are highly dependent on the operating conditions and catalyst composition. At longer times-on-stream, new peaks are detected, in agreement with the presence of new bands observed by FTIR spectroscopy; these can correspond to the formation of new species and modifications of those previously formed due to processes such as oxidation of lateral groups of the aromatic rings. The presence of uncoated TiO_2 can account for a stronger interaction between the molecules and the catalyst surface (22), making carbon–carbon bonds weaker, facilitating their oxidation and leading to lower T_{max} values.

Figures 6 and 7 show the oxygen consumption for samples tested under different operating conditions. This increases with time-on-stream, attaining generally a constant level after one hour under reaction conditions. For 533 K, no constant value is observed but, for longer times of exposure to reaction conditions, a decrease in the rate of oxygen consumption could be detected. Considering that the oxygen consumption is closely related to the amount of residue deposited on the surface, results show that processes for residue consumption, such as desorption or oxidation to CO_2, must also be considered.

The amount of heavy compounds formed is highly dependent on the catalyst surface features and experimental conditions under which each sample was tested. Smaller amounts of those compounds were obtained at higher temperatures and higher contact times between the reactant mixture and the catalyst bed, which is in agreement with kinetic results previously reported (22). For the same experimental conditions, amounts of residue are higher for 0.6% V_2O_5/TiO_2. The presence of Lewis acid sites, due to uncovered TiO_2, can give rise to a stronger interaction between the surface and the aromatic intermediates, enhancing reaction between these adsorbed species.

The comparison of values observed for o-xylene and o-tolualdehyde oxidation indicates that o-xylene can be an important source of heavy by-products; for the same experimental conditions, the amounts of residue obtained using o-tolualdehyde are lower than those for o-xylene oxidation.

Mass Spectrometry Studies

The analysis by mass spectrometry of the residue extracted from the catalysts allows a better understanding of its composition. The spectrum of the sample containing anthracene over 1% V_2O_5/TiO_2 shows peaks at *m/z* values of 178, 152, 89, and 76, indicating that the process used for sample dissolution does not lead to modifications of aromatic rings. Thus, the mass spectra obtained provide information about the number of aromatic rings present in the residue molecules; however, the exact knowledge of their structure is difficult to obtain since, after the treatment with HF, some of the lateral groups of the aromatic rings can undergo modification.

The highest *m/z* values obtained for residue deposited on the samples tested at 1.6×10^{-5} kg_{cat} dm^{-3} h are presented in Table 1. These were found to vary both with the catalyst composition and the reaction temperature. In fact, higher *m/z* values are associated with molecules adsorbed on 0.6% V_2O_5/TiO_2; the stronger interaction between its surface and the aromatic intermediates would make their desorption difficult, facilitating the oxidation of their lateral groups. On the other hand, samples tested at lower reaction temperatures, that were found to favor reaction between

TABLE 1

Highest *m/z* Values Obtained by Mass Spectrometry for Carbonaceous Deposits Formed over V_2O_5/TiO_2 Samples Tested at Different Temperatures (T_R) and after 4 h of Exposure to Reaction Conditions

Catalyst	$T_R = 533$ K	$T_R = 613$ K
o-Xylene oxidation		
0.6% V_2O_5/TiO_2	307	255
1% V_2O_5/TiO_2	293	213
5% V_2O_5/TiO_2	241	223
o-Tolualdehyde oxidation		
1% V_2O_5/TiO_2	293	213

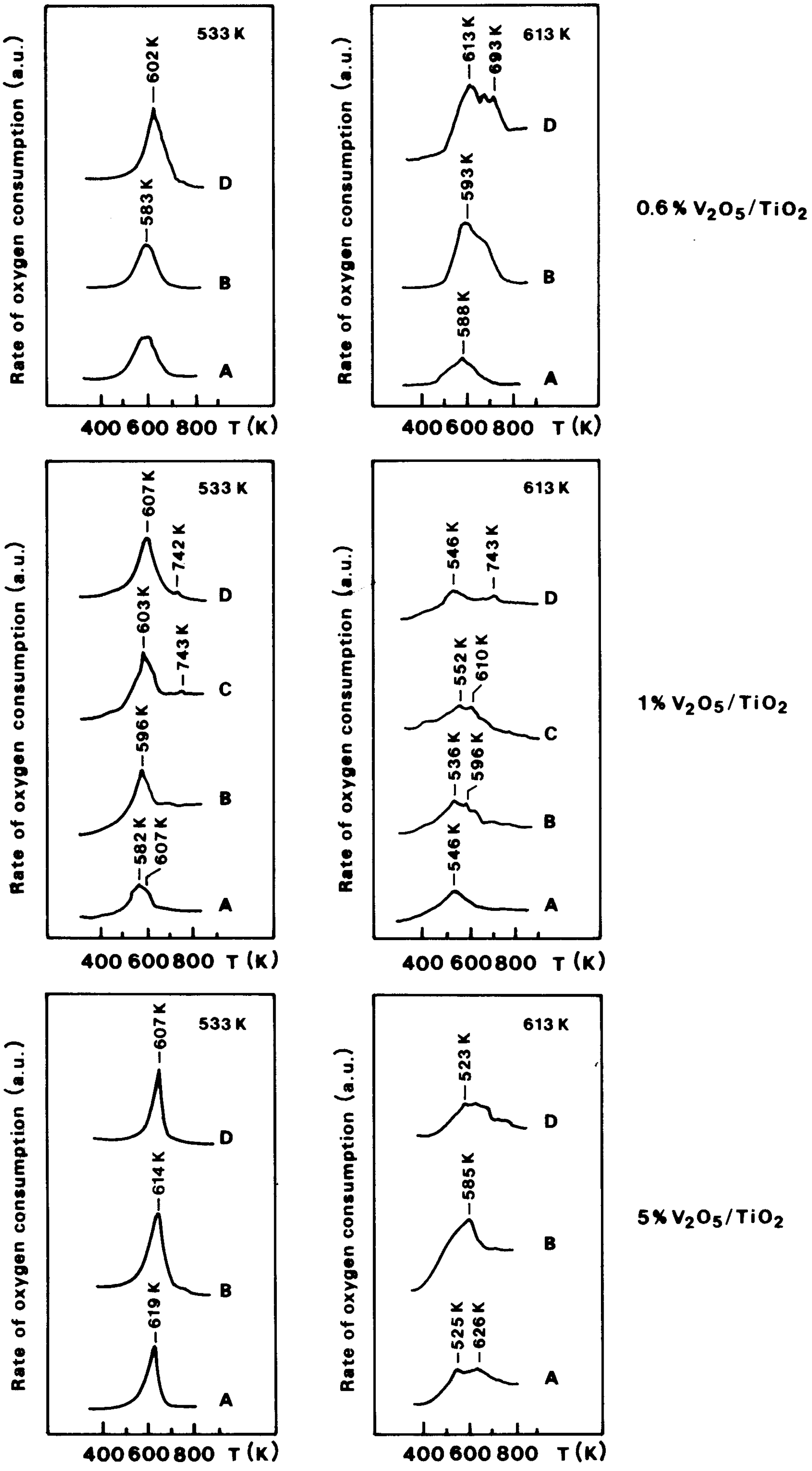


FIG. 5. TPO profiles for 0.6, 1, and 5% V_2O_5/TiO_2 samples tested for o-xylene oxidation at different temperatures. Time of exposure to reaction conditions: A, 0.25 h; B, 1 h; C, 2.5 h; D, 4 h.

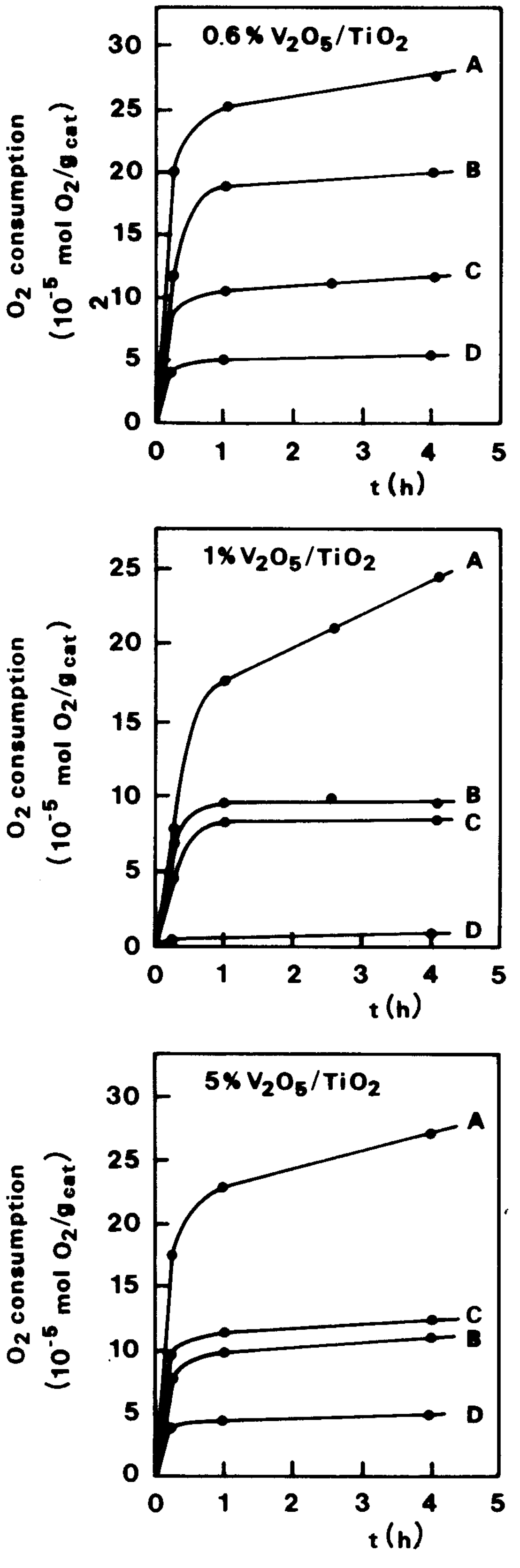


FIG. 6. Oxygen consumption obtained by TPO versus the time samples are exposed to o-xylene/air mixtures: A, W/F = 1.6 × 10^{-5} kg_{cat} dm^{-3} h; T_R = 533 K; B, W/F = 1.6 × 10^{-5} kg_{cat} dm^{-3} h; T_R = 613 K; C, W/F = 2.3 × 10^{-4} kg_{cat} dm^{-3} h; T_R = 533 K; D, W/F = 2.3 × 10^{-4} kg_{cat} dm^{-3} h; T_R = 613 K.

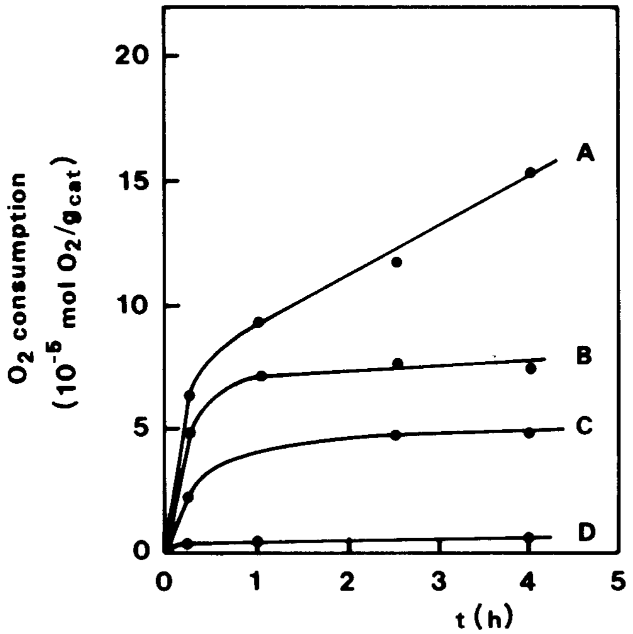


FIG. 7. Oxygen consumption obtained by TPO versus the time 1% V_2O_5/TiO_2 is exposed to o-tolualdehyde/air mixtures. Symbols as in Fig. 6.

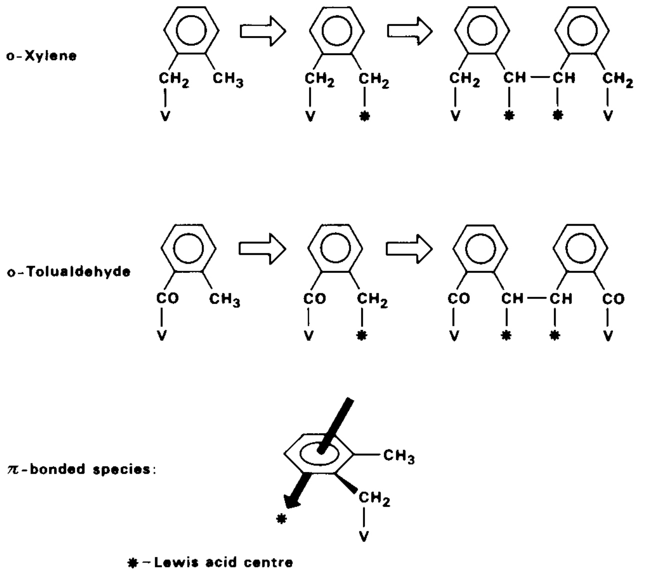
adsorbed species (22), give higher *m*/*z* values. However, the results indicate that the molecules detected do not contain more than two aromatic rings.

MECHANISM OF RESIDUE FORMATION

The formation of an organic residue during the oxidation of o-xylene has been established. It can either stay on the catalyst surface, or undergo total oxidation, or desorb and condense on the cooler parts of the system. Complete knowledge of the structure of the residue is difficult to obtain due to the low levels detected and to the occurrence of complex mixtures. However, molecules detected by mass spectrometry contain no more than two aromatic rings, formed by reaction between two adsorbed species, such as those obtained by the chemisorption of o-xylene, which was proven to be an important source of such compounds. Similar products are also formed in the oxidation of o-tolualdehyde.

The formation of an adsorbed residue is favored at lower W/F and lower temperatures (viz. at low conversion), while selective and total oxidation is enhanced at higher temperatures (viz. high conversion). Residue formation is therefore at least partly a characteristic of a partially reduced V_2O_5 surface, such as is found at the inlet side of the catalyst bed where the O_2/o-xylene ratio (which increases with conversion) is insufficient to keep the surface fully oxidized. A second factor encouraging residue formation is the presence on uncoated TiO_2 surface of Lewis acid centers; on these, and on V^{3+} or V^{4+} ions, there can be a stronger interaction with aromatic intermediates than on oxidized VO_x surface; this will make desorption difficult and will enhance formation of dimers by reaction between adjacent adsorbed species. Third, the presence crystalline V_2O_5 can also have some influence in residue formation, for its characteristics, as shown by FTlR spectra of used samples, vary when the V_2O_5 loading increases from 1 to 5%.

A possible mechanism for dimerization has been suggested before (11); a modified version is



together with a corresponding process, applying to o-tolualdehyde. Its main feature is the simultaneous bonding of both alkyl groups to reduced V or to Ti^{4+} sites before either has begun to be oxidized; it is unlikely that such species will revert to those from which selective oxidation products may arise, so under low conversion conditions their principal fate will be to form dimers, or higher polymers. Ultimately they can either only desorb or become oxidized to CO_2. A further factor which may contribute to the strong retention of these species is π-bonding of the aromatic ring to an adjacent site (this effect being either additional to or a substitute for the σ-bonded adsorption), as is also shown in the diagram above. This bond has the same character as that formed, for example, between benzene and $AlCl_3$. Partial oxidation of strongly-retained species may occur before desorption, since changes in the FTIR spectra are observed with increasing reaction time.

CONCLUSIONS

The characteristics and the amount of the adsorbed residue are highly dependent on the catalyst composition and operating conditions used. The formation of these products is favored at lower W/F and lower temperatures; other processes, such as selective and total oxidation, are enhanced at higher temperatures. The presence of uncoated TiO_2, exhibiting Lewis acid sites, can lead to a stronger interaction between aromatic intermediates and the catalyst surface, making desorption difficult and enhancing the reaction between adsorbed species. The Brønsted acid sites of the crystalline V_2O_5 can also influence the residue's characteristics, FTIR spectra of used samples showing weaker C−O, $>CH_2$, and $-CH_3$ bands for higher V_2O_5 loading. Lateral groups of dimers which stay on the surface can undergo partial oxidation, thereby causing the structure of the adsorbed residue to vary with the time that samples stayed under reaction conditions.

ACKNOWLEDGMENTS

The authors are grateful to the British Council and Junta Nacional de Investigação Científica e Tecnológica (JNICT) for financial support. The assistance of Mr. H. Dee in obtaining the mass spectrometry data is gratefully acknowledged.

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