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FT-IR Study of Structure of Toluene Adsorbed on Vanadium-Titanium Oxide

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The adsorption of toluene on V−Ti oxide prepared by gas-phase method (the Vanadium content ranged from 2.1 to 5.6 wt%) and the role of surface acidic and basic sites have been studied by Fourier-transform infrared spectroscopy. From the adsorption of toluene, perdeuterotoluene and benzene on various V−Ti oxides together with titania, it is found that toluene is bonded as π − complex to the vanadium ion with its benzene ring parallel to the surface. The CH_3 groups of π − complex are dehydrogenated by the V = O species to form the benzyl species and the V−OH species, and the π − complex is interacted with surface hydroxyl groups if there is a surface free hydroxyl group adjacent to the site containing the π − complex.

Key Words
FT−IR study,
Structure,
Toluene,
Adsorption,
V−Ti oxide.

INTRODUCTION

The selective gas phase oxidation of hydrocarbon over oxidic catalysts has been extensively studied. Especially vanadium oxide catalysts are well known for the practical use of their high selectivity and activity. A number of these investigations concern kinetic measurements or tracer experiments, which have been performed to obtain information on the mechanism of the oxidation reaction. Additional and sometimes even more direct evidence can often be obtained by studying the interaction of the reactant and/or its products with the surface of catalyst using infrared spectroscopy. Infrared spectroscopy appears to be most suitable for the purpose of observing the adsorbed species during the reaction.

In the previous works we studied the reaction intermediates in the oxidation of alkenes (1,2), alkynes (3,4), and alcohols (5−9) on oxide catalysts by infrared techniques. Only a limited number of infrared studies on the identification of surface structure formed in the oxidation of aromatic hydrocarbons have appeared in the literature (10). In the present work we therefore employed Fourier-transform infrared spectroscopy in the study concerning the structure of toluene over vanadium oxide catalysts, and examined the development of fast algorithms for the band shape analysis and the data acquisition system of the infrared spectra of

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adsorbed species using a small computer system with a high-resolution graphics display.

MATERIALS AND METHODS

The titania (Japan Aerosil Co., P−25) was used as a support. A gas phase preparation method was used to support vanadium oxide. After disks of titania (20−mm diameter, ca. 100 mg) had been placed in a glass tube, the disk temperature was slowly increased from room temperature to 723 K under evacuation and kept at that temperature for several hours. Then a flow of water-saturated nitrogen was passed through disks at 298 K for 2 h, followed by degassing at 473 K for 4h. After that, circulation of nitrogen, which was saturated with vanadium oxychloride vapor, followed by circulation of water-saturated nitrogen was repeated several times. Finally, the excess vanadium oxychloride was removed by evacuation at 670 K. The vandium contents, which were measured by the N-BPHA method (JIS G1221), ranged from 2.1 wt% to 5.6 wt% (GVTi−2.1 − GVTi−5.6). The physical parameters of those catalysts are listed in table 1.

Toluene, benzene (Wako Pure Chemical Industries LTD., SSG or SG) and $[^2H_8]$ toluene (Merck Co., 99.7%) were distilled several times under vacuum before use.

The apparatus used was a conventional closed-circulation system equipped with an infrared cell for spectroscopic study. The infrared cell was a quartz tube 2.5 cm diameter and 40 cm in length. The KRS−5 windows were sealed to the cell with wax. The sample disk was held in a quartz disk holder and was suspended by a platinum wire in the cell. The disk could be moved vertically between the lower window section and the upper furnace section. The temperature of the disk was measured by a calibrated thermocouple fixed to furnace section of the cell.

The catalyst disk was heated to 673 K under evacuation and kept at that temperature under flow of oxygen (ca.

Table 1: Physical properties of GVTi catalysts.

Catalyst	Repeat number[a]	V_2O_5 (wt%)	Surface area[b] (m^2/g)
GVTi-2.1	1	2.1	50
GVTi-3.3	2	3.3	50
GVTi-5.6	8	5.6	30

[a] repeat number of $VOCl_3$ circulation.
[b] measured by the BET method.

4 kPa) for 2 h. This treatment was repeated several times before each experiment.

Fourier-transform infrared spectra were recorded at ambient temperature before and after each treatment of the catalyst disk, such as heating or admission of reactant; with the use of a Shimadzu FTIR−4000 operating at 2 cm^{-1} resolution and at single beam mode. This could prevent a temperature rise of the catalyst disk. After 100 accumulations had been used the data were transferred on an IEEE−488 bus line to a master computer (PC−9801 VX2, NEC). Spectra were sampled at suitable intervals (1−5 cm^{-1}) and stored in disk files. In order to obtain quantitative information on the spectral behavior, some of the spectra were subtracted and deconvoluted by using a data acquisition system. The details of the data acquisition and analysis system were described previously (11,12).

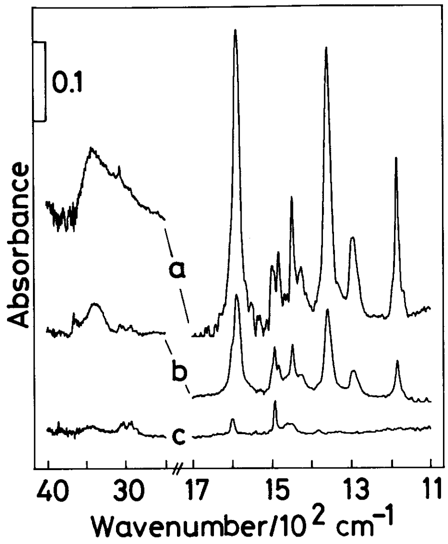

Figure 1. FT-IR spectra of toluene adsorbed: (a) on GVTi−5.6 after introduction of toluene (0.07 cm^3/g) followed by 1 h evacuation at 293 K, (b) on GVTi−2.1 after 10 min evacuation at 293 K, (c) on TiO_2 after adsorption of toluene followed by 30 min evacuation at 293 K.

RESULTS

1. Adsorption of Toluene on GVTi−5.6, GVTi−2.1, and TiO_2

Fig. 1 shows FT−IR spectra of toluene adsorbed on catalysts after subtraction of catalyst itself. A small amount of toluene (0.07cm^3/g) was introduced onto GVTi−5.6 at room temperature, followed by evacuation at room temperature for 1 h. A number of bands appeared in the regions of stretching and bending modes (Fig. 1a). The broad band at ca. 3450 cm^{-1} is due to the ν (O−H) of hydrogen bonded species. The bands near 3000 cm^{-1} are due to ν (C−H) in the benzene ring of toluene adsorbed. The bands in the region 1700 − 1100 cm^{-1} are assigned to the ν (C=C) of the skeletal ring or the δ (C−H) of the CH_3 groups.

In the case of GVTi−2.1 (Fig. 1b), only weak bands remained at almost the same positions as observed on GVTi−5.6, while on TiO_2 toluene was easily removed by evacuation at room temperature for 30 min (Fig. 1c). The results suggest that the surface vanadate species are active sites for the adsorbed toluene.

The bands due to toluene adsorbed on GVTi−2.1 are much weaker than that on GVTi−5.6 (Fig. 1a, b), showing that the concentration of adsorbed sites on GVTi−2.1 is smaller than that on GVTi−5.6. However, on GVTi−2.1, there are two bands at ca. 3700 and ca. 3400 cm^{-1} in the ν (O—H) stretching region. The band at ca. 3700 cm^{-1} must be assigned to the surface free hydroxyl groups on TiO_2, being in agreement with that observed on TiO_2 (7). This suggests that the GVTi—2.1 catalyst is not fully covered with vanadate species.

2. Adsorption of [$^2H_8$]toluene on GVTi—3.3

In order to clarify the interaction of surface OH groups with adsorbed toluene, a similar experiment was carried out using [$^2H_8$]toluene. The spectral changes with increasing time of adsorption were recorded, the resulting spectra being shown in Fig. 2. It must be noted that bands near 2350 cm^{-1} are due to carbon dioxide molecules in air owing to the measurements by a single beam mode. A number of bands were observed immediately after introduction of [$^2H_8$]toluene (0.07 cm^3/g) at room temperature (Fig. 2a). The broad band at 3400 cm^{-1} is due to ν (O—H) of hydrogen bonded species between [$^2H_8$]toluene and surface hydroxyl group of GVTi-3.3. The bands at 2470 cm^{-1} and at 2278 cm^{-1} are due to ν (O—D) of the hydrogen bonded species and ν (C—D) in the benzene ring, respectively. The bands at 2240, 2212, and 2120 cm^{-1} are assigned to $\nu_{as}(CD_3)$, $\nu_s(CD_3)$, and $\nu(CD_2)$ of [$^2H_8$]toluene adsorbed, respectively. In the region 1700 – 1200 cm^{-1} only skeletal ring vibrations are expected in the spectra due to isotopic shifts for δ (C—D) bands(13).

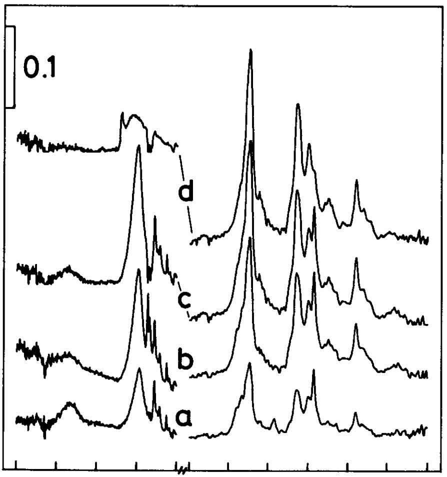

Figure 2. FT-IR spectra of [$^2H_8$]toluene adsorbed on GVTi—3.3 at room temperature: (a) immediately after introduction of [$^2H_8$]toluene (0.07 cm^3/g), (b) followed by 30 min, (c) 2 h, and (d) followed by 1 h evacuation.

As increasing the time of adsorption the broad band at 2470 cm^{-1} as well as the bands in the region 1700—1300 cm^{-1} intensified, while the intensities of the bands at 2212 and 2120 cm^{-1} reduced (Fig. 2a—c). During this process the bands at 3450 and 2278 cm^{-1} remained unchanged in intensity. On evacuation at room temperature for 1 h the bands at 2278 and 2212 cm^{-1} together with a broad band at 3450 cm^{-1} disappeared and the band at 2470 cm^{-1} reduced in intensity, while a new band appeared at 2570 cm^{-1} (Fig. 2d). This suggests that partial H-D exchange reaction occurred to form surface OD groups, which show the band at 2570 cm^{-1}. The infrared bands of toluene adsorbed on GVTi catalysts together with liquid toluene (14) are summarized in Table 2.

3. Adsorption of Benzene on GVTi–5.6

In a separate experiment the adsorption of benzene on GVTi–5.6 was investigated in order to clarify the orientation of benzene ring on the surface. FT–IR spectra of benzene adsorbed on GVTi–5.6 exhibit a number of bands in the CH stretching and bending regions together with hydrogen bonded OH (Fig. 3a). After the catalyst was evacuated at room temperature for 0.5 h, most of these bands reduced in intensity and some of them shifted slightly to lower wavenumber (Fig. 3b). The bands at 1583, 1483, 1450, and 1293 cm^{-1} are assigned to B–I, B–IIa, B–IIb, and B–III mode in the skeletal ring vibrations, respectively (15). The band at 1358 cm^{-1} is due to δ (C–H) in-plane. From comparison with the corresponding bands of liquid benzene (14) the bands at 1583 and

Table 2: Wavenumber (cm^{-1}) of the infrared bands of toluene adsorbed on GTVi catalyst.

toluene	$[^2H_8]$toluene	liquid toluene[a]	vibrational mode[b]
3450	2470	-	ν(O-H) or ν(O-D)
3070	2278	3070	ν(C-H) or ν(C-D)
	2240	2910	$\nu_{as}(CH_3)$ or $\nu_{as}(CD_3)$
	2212	2860	$\nu_s(CH_3)$ or $\nu_s(CD_3)$
	2120		
1590	1548	1607	B-I
1500	1400	1496	B-IIa
1485	1378		B-IIb
1450		1460	$\delta_{as}(CH_3)$
1428			
1360		1378	$\delta_s(CH_3)$
1295	1280	1310	B-III
1190		1212	δ(C-H) in-plane

[a] in ref. (14).

[b] in ref. (15).

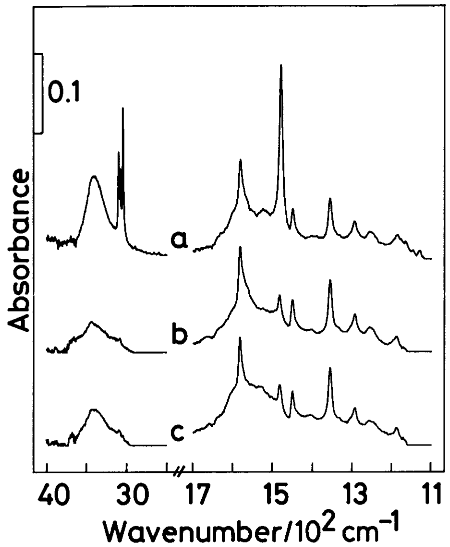

Figure 3. FT-IR spectra of benzene adsorbed on GVTi−5.6: (a) 30 min after introduction of benzene (2.6 kPa) at 293 K, (b) followed by 30 min evacuation at 293 K, and (C) followed by 30 min under circulation of oxygen (2 kPa) at 393 K.

1483 cm^{-1} are shifted to lower wavenumber about 10 to 3 cm^{-1}.

After increasing the temperature of the disk to 393 K for 0.5 h under circulation of oxygen (2.6 kPa), new bands appeared at 1600, 1550, and 1400 cm^{-1} and the broad band at 3450 cm^{-1} was intensified (Fig. 3c). This shows that adsorbed benzene was dehydrogenated by GVTi−5.6 to form surface hydroxyl groups. This also shows that the surface sites are strong enough to abstract the hydrogen from the benzene ring at relatively low temperature.

DISCUSSION

The band due to hydrogen bonded OH (ca. 3450 cm^{-1}) appeared on all the catalysts irrespective of vanadium content. This suggests that adsorbed toluene interacts with the surface oxygen or the hydroxyl group of each catalyst. In addition, considering that GVT−5.6 itself shows only weak band due to hydroxyl groups, some OH groups were formed on the adsorption of toluene.

The results on TiO_2 were in agreement with that of Graham et al (16), who concluded that toluene interacts weakly with the surface hydroxyl groups on rutile. These species are easily removed by evacuation at room temperature (Fig. 1c).

As just mentioned above, the bands due to the vibrations of the aromatic ring (1590 and 1485 cm^{-1}) in toluene adsorbed on GVTi catalysts showed the lower shift (Fig. 1a, b). This suggests that a π − complex of toluene is formed on GVTi catalysts as reported on montmorillonite (17) and on zinc oxide (18). However, the corresponding bands on TiO_2 did not change in the position compared with that in liquid toluene (Fig. 1c), suggesting that π − complexes of toluene are not formed on TiO_2.

In the previous works we reported that vanadium ions and oxygen in the surface vanadate species on GVTi catalysts act as the Lewis-acid and basic sites, respectively (8) and that the carrier TiO_2 exhibits no strong basicity (19). Thus, it is concluded that toluene is adsorbed on the vanadium ion to form the π − complex as well as the hydrogen bonded species. Accordingly, the π − complex is adsorbed on the Lewis-acid site, while there are two posibilities for formation of the hydrogen bonded species. The first is due to the basic site; i.e., the surface V=O species. The second is due to the Brönsted-acid site; i.e., the surface V–OH species.

From the results in Fig. 2, on increasing the period of adsorption, the bands of stretching vibration of methyl group reduced in intensity, while the band of ν (O–D) together with the bands of skeletal ring vibration were intensified. In addition, the ν (C–D) in benzene ring remained unchanged. These behavior suggests that methyl group of toluene is dehydrogenated by surface oxygen to form the hydroxyl group and the dissociated benzyl species of toluene on the surface.

Chang and Kokes reported that toluene adsorbed on ZnO undergo dissociation by the basic site to form the benzyl species via the rupture of the methyl C-H bond (18). This may occur more easily on the GVTi catalysts, since their basicity must be strong enough to abstract the hydrogen from the methyl group of toluene adsorbed (8). They also suggested that the benzyl species on ZnO was adsorbed with its benzene ring parallel to the surface because of lower wavenumber shift of aromatic ring during the dissociation. Although the corresponding shift did not occur during the dehydrogenation of π – complex of $[^2H_8]$toluene (Fig. 2), this is also possible on the GVTi catalysts from the results of benzene adsorption on GVTi–5.6.

As shown in Fig. 3 benzene is adsorbed weakly on GVTi–5.6 to form hydrogen bonded species. Although the value of wavenumber shifts of skeletal vibrations of benzene on GVTi–5.6 are small in comparison with the case of adsorbed toluene, the π – complex of benzene may be present on GVTi–5.6. On α – Fe_2O_3 benzene was adsorbed on surface Lewis-acid site as π – complex with its benzene ring parallel to the surface (20). Thus, it is concluded that benzene is adsorbed on surface Lewis-acid site of GVTi–5.6 as the π – complex with its ring parallel to the surface. The π – complex of toluene is adsorbed more strongly than that of benzene since toluene has a high π – electron density owing to its methyl group in aromatic ring.

Accordingly, it is concluded that the surface reaction proceeds as shown in Fig. 4. First, toluene is bonded as π – complex to the Lewis-acid site, i.e., vanadium ion, with its benzene ring parallel to the surface, secondly, the CH_3 group of π – complex is dehydrogenated by the basic site, i. e., the V=O species of vanadate, to form the benzyl species and the V–OH species. If there is a surface free hydroxyl group adjacent to the site

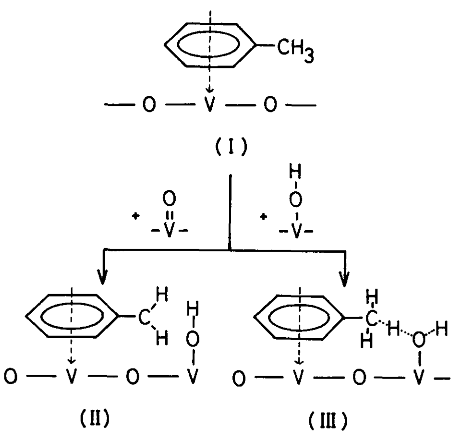

Figure 4. Scheme of surface reaction on GVTi catalyst: (I) π – complex, (II) dissociative benzyl species, and (III) hydrogen bonded species.

containing the π – complex, its hydrogen atom in the methyl group interacts with oxygen atom in the hydroxyl group to form the hydrogen bonded species.

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