

분무 열분해법을 이용해 제조된 VO_x/Mesoporous Titania 상에서 1,2-dichlorobenzene의 분해반응에 대한 *in situ* FT-IR 연구

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In situ FT-IR Study of 1,2-dichlorobenzene Decomposition over VO_x/Mesoporous Titania by Prepared Spray Pyrolysis

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본 연구에서는 분무 열분해 방법으로 제조된 메조기공 V₂O₅/TiO₂ 촉매 상에서 1,2-dichlorobenzene (1,2-DCB)의 표면 활성종을 파악하고자 하였다. 이를 위하여 *in situ* FT-IR cell을 이용하여 1,2-DCB의 흡착/탈착을 수행하였다. 또한 기존의 TiO₂와 incipient wetness로 제조된 V₂O₅/TiO₂ 상의 흡착종들과의 비교도 함께 수행되었다.

In this study, surface-adsorbed species of 1,2-dichlorobenzene (1,2-DCB) on mesoporous V₂O₅/TiO₂ catalysts synthesized by spray pyrolysis were investigated through the adsorption/desorption performed using *in situ* FT-IR cell. Also, the comparison of adsorbed species with TiO₂ and V₂O₅/TiO₂ synthesized by the incipient wetness was carried out.

Keywords: *in situ* FT-IR, spray pyrolysis, mesoporous V₂O₅/TiO₂

1. Introduction

Persistent organic pollutants (POPs) was emitted as byproducts from many industrial processes[1-3]. To reduce POPs emissions, especially those of chlorinated compounds, much effort has been performed. One of the efficient technologies for the decomposition of organic compounds is catalytic oxidation[4-6]. Until now, TiO₂-based V₂O₅/WO₃, noble metals supported on various oxides and zeolites have been used as the catalysts for the oxidation of chlorinated POPs. Among them, V₂O₅/TiO₂, which has been used for the removal of NO_x, is known to have the high catalytic activity for the oxidation of chlorinated organic pollutants[7,8]. Meanwhile, the catalytic activity/selectivity of the V₂O₅/TiO₂ system strongly depends on the synthesis methods such as crystallographic form of titania, the vanadium loading (quantity and dispersion) and calcinations temperature.

In our previous works, mesoporous V₂O₅/TiO₂ particles were prepared by spray pyrolysis and applied to the catalytic oxidation of 1,2-dichlorobenzene (1,2-DCB)[9,10]. However, the study of surface adsorbed species has not been examined. In this study, we performed

in-situ FT-IR to investigate the surface species of 1,2-DCB on mesoporous V₂O₅/TiO₂ particle.

2. Experimental

2.1. Synthesis of Catalyst

Titanium tetraisopropoxide (TTIP, Aldrich) and ammonium metavanadate (NH₄VO₃, Aldrich) were used as the precursors of TiO₂ and V₂O₅, respectively. P123 ((ethylene oxide)₂₀-(propyleneoxide)₇₀-(ethyleneoxide)₂₀, Aldrich) was used as a structure-directing agent. For more detailed synthesis procedures of catalysts used for this study, one can refer to the previous papers[9,10].

2.2. *In situ* FT-IR

Figure 1 shows the schematic diagram of *in situ* FT-IR apparatus. The synthesized V₂O₅/TiO₂ particles (0.032 g) was pressed to make disk-shaped catalysts, which was loaded on *in situ* FT-IR cell. The cell temperature was elevated to 350 °C for pretreatment, flowing 50 mL/min of mixture gas (5% O₂/He) for 2 h and He gas for 30 min, respectively. After the FT-IR cells were cooled down to room temperature, a background spectrum was obtained. For the adsorption of 1,2-DCB, 50

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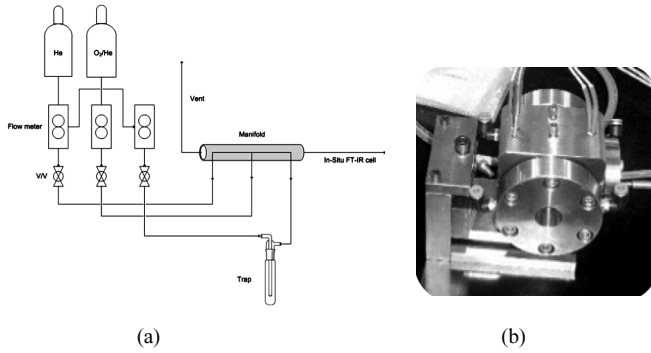


Figure 1. Apparatus for (a) Adsorption of 1,2-DCB and (b) *In situ* FT-IR cell.

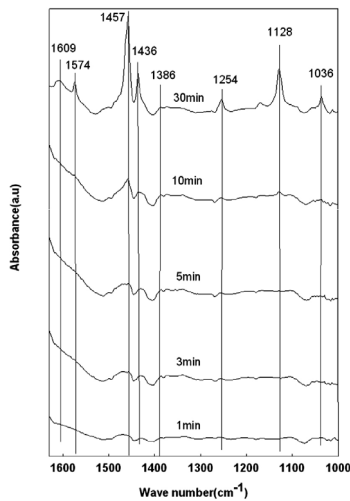


Figure 2. FT-IR spectra of the species arising from the adsorption of 1,2-DCB at 298 K on TiO₂ catalyst

mL/min of 1,2-DCB diluted with He was fed to catalyst surface at 100 °C. Then FT-IR spectra were obtained at 1, 3, 5, 10, and 30 min, respectively.

For temperature programmed desorption, 50 mL/min of He was flowed to purge the catalyst surface for 30 min. Then FT-IR spectra of the desorption of 1,2-DCB were obtained at 100, 150, and 200 °C, respectively.

The experiments for high temperature adsorption of 1,2-DCB and temperature programmed desorption were carried out in the temperature range from 200 °C to 350 °C. After 1,2-DCB diluted with He was injected into the catalyst surface at 200 °C, the catalyst surface was purged using He for 30 min. Thereafter, FT-IR spectra of the desorbed 1,2-DCB were monitored with increasing the cell temperature from 200 °C to 350 °C.

3. Results and Discussion

Surface adsorbed species were obtained using *in situ* FT-IR by adsorbing or desorbing 1,2-DCB on three kind of catalysts such as TiO₂, V₂O₅ (5 wt%)/TiO₂ made by spray pyrolysis and V₂O₅ (5 wt%)/TiO₂ made by incipient wetness. Figure 2 shows the FT-IR spectrum for the

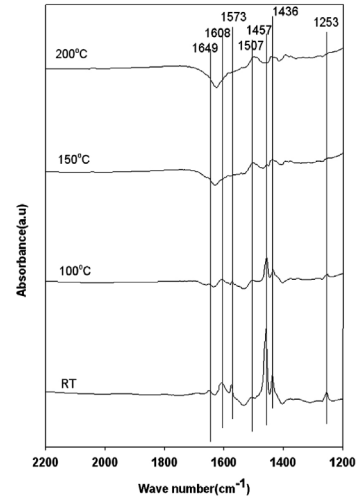


Figure 3. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 298 K for 30 min on TiO₂ catalyst.

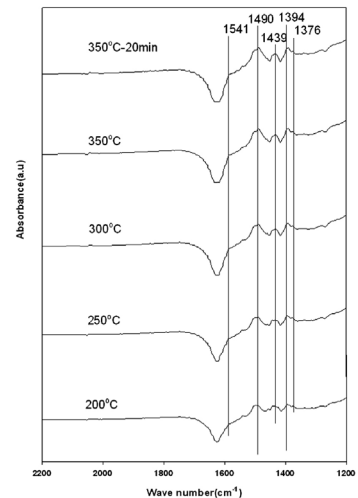


Figure 4. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 200 °C on TiO₂ catalyst.

adsorption of 1,2-DCB vapor on pure TiO₂ catalysts at room temperature. Figure 3 shows the FT-IR results for the desorption of 1,2-DCB from TiO₂ catalyst, elevating the cell temperature from room temperature to 200 °C. For adsorption spectra of 1,2-DCB, the most obvious peaks were observed at 1436 and 1457 cm⁻¹, respectively. The peaks at 1036, 1128, 1254, 1386, 1574, and 1609 cm⁻¹ grew up. Peaks at 1400~1650 cm⁻¹ can be assigned to C-C bond stretching in aromatic compounds. As shown in Figure 3, with increasing the temperature, a peak at 1507 cm⁻¹ appears obviously.

Figure 4 shows the FT-IR results of high temperature adsorption/desorption of 1,2-DCB on TiO₂ catalyst. 1,2-DCB was adsorbed at 200 °C and then the cell temperature increased to 350 °C under flowing the He gas. As temperature increases, the intensity of peaks at 1394, 1376, and 1490 cm⁻¹ which can be assigned to carboxylate grew up[11-13].

The results of adsorption/desorption of 1,2-DCB on V₂O₅ (5 wt%)/TiO₂ made by spray pyrolysis were shown in Figures 5~7. The Figures

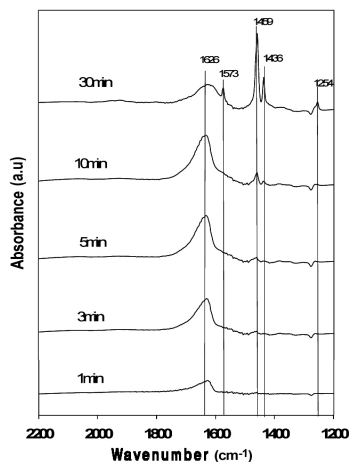


Figure 5. FT-IR spectra of the species arising from the adsorption of 1,2-DCB at 298 K on V_2O_5 (5 wt%)/ TiO_2 catalyst synthesized by spray pyrolysis.

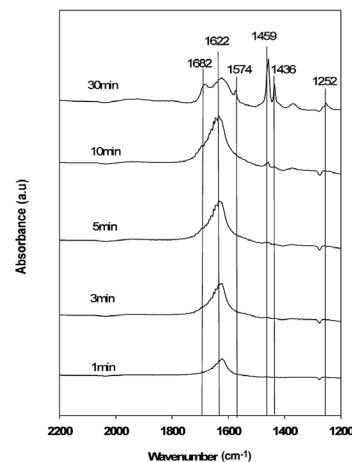


Figure 8. FT-IR spectra of the species arising from the adsorption of 1,2-DCB at 298 K on V_2O_5 (5 wt%)/ TiO_2 catalyst synthesized by incipient wetness method.

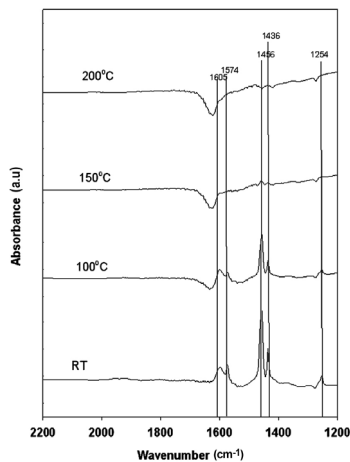


Figure 6. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 298 K for 30 min on V_2O_5 (5 wt%)/ TiO_2 catalyst synthesized by spray pyrolysis.

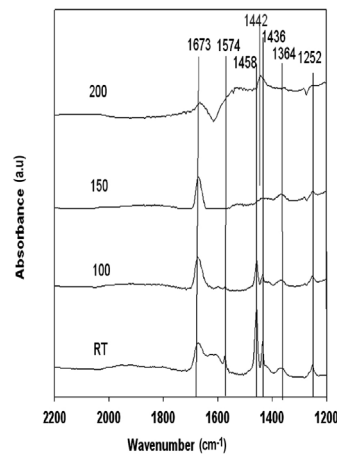


Figure 9. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 298 K for 30 min on V_2O_5 (5 wt%)/ TiO_2 catalyst synthesized by incipient wetness method.

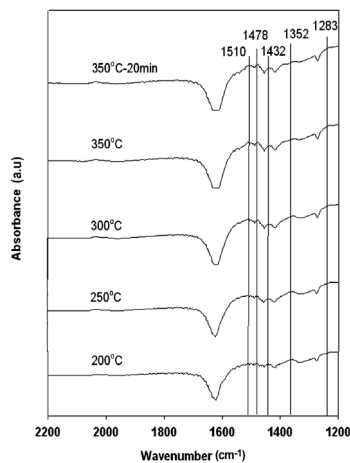


Figure 7. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 200 °C on V_2O_5 (5 wt%)/ TiO_2 catalyst synthesized by spray pyrolysis.

showed similar tendency with those of adsorption/desorption on TiO_2 . However, V_2O_5 (5 wt%)/ TiO_2 made by incipient wetness showed a different behavior with those of above two kind of catalysts. That is, the peak at $1441 \sim 1442 \text{ cm}^{-1}$, which was not observable obviously for TiO_2 and V_2O_5 (5 wt%)/ TiO_2 catalysts prepared by spray pyrolysis, became obvious for V_2O_5 (5 wt%)/ TiO_2 made by incipient wetness as shown in Figures 8~10 showing the results of desorption of 1,2-DCB. This peak was known to carboxylate species which was produced by partial oxidation by oxygen species on catalyst surface[11-13].

Because, as shown above, much vanadium existed on catalyst surface synthesized by incipient wetness rather than by spray pyrolysis, these vanadium may affect the formation of partially oxidized carboxylate species.

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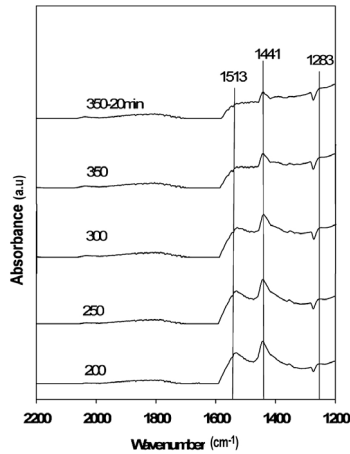


Figure 10. FT-IR spectra of the species during desorption of 1,2-DCB under He flow after adsorption of 1,2-DCB at 200 °C on V₂O₅ (5 wt%)/TiO₂ catalyst synthesized by incipient wetness method.

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