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Investigation of acid sites on $V_2O_5/TiO_2(A)$ Catalysts by FTIR with Adsorption of Pyridine

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The $V_2O_5/TiO_2(A)$ catalysts were prepared by the grafting and their Brönsted and Lewis acid sites were investigated with pyridine adsorption by using FTIR Spectroscopy. The results obtained showed that monolayer or less coverage of the surface of the support, $TiO_2(A)$, took place up to V_2O_5 content of 11.88 %. When V_2O_5 amount was higher than 11.88 %, the support was covered as multilayer. Pyridine adsorption studies showed that the number of the Lewis acid sites of the $V_2O_5/TiO_2(A)$ catalysts decreased with increasing of V_2O_5 amount. The number of the Brönsted acid sites increased with increasing V_2O_5 content, reached a maximum at 11.88 wt. % of V_2O_5 and then began to decrease with increased V_2O_5 content.

Key Words: $V_2O_5/TiO_2(A)$ catalyst, Lewis acid site, Brönsted acid site, pyridine adsorption

Introduction

In industry, $V_2O_5/TiO_2(A)$ catalysts are used particularly in oxidation of oxylene to produce phthalic anhydride and in partial oxidation of benzene to produce maleic anhydride^{1,2}. The catalytic properties of these catalysts depend on the amount of V_2O_5 covered on the surface of support material, $TiO_2(A)$. All $V_2O_5/TiO_2(A)$ catalysts, the catalytically active component, V_2O_5 , covers the support material, $TiO_2(A)$, as a monolayer are highly selective during the oxidation of oxylene.

In our previous work, $V_2O_5/TiO_2(A)$ catalysts were prepared by the grafting method and their acidic properties were investigated with NH_3 adsorption by FTIR spectroscopic technique³. In the present work, $V_2O_5/TiO_2(A)$ catalysts were prepared by using the same method and their acidic properties were investigated with pyridine adsorption.

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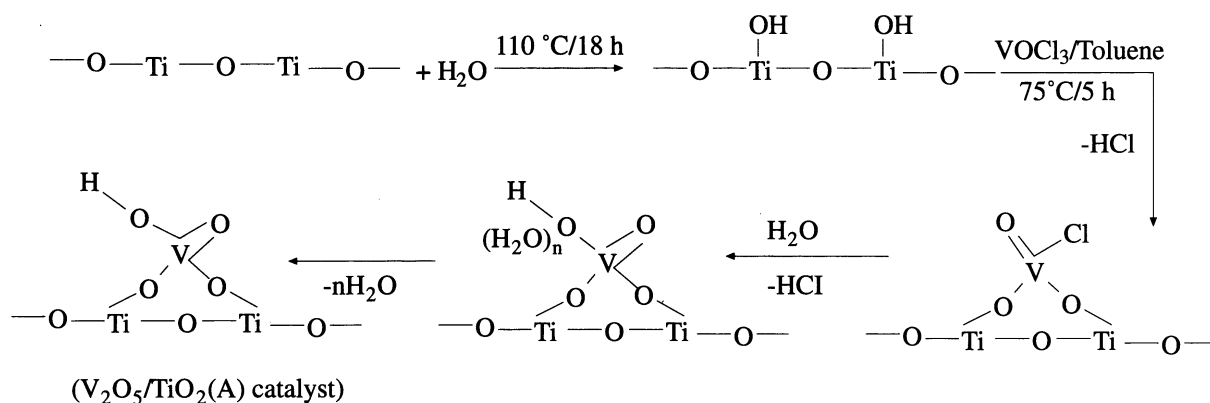
Experimental Section

Catalyst Preparation

The support material, TiO_2 (anatase, BET surface area $92\text{ m}^2\text{g}^{-1}$), was wetted with bidistilled water and dried at 110°C for 18 h and then it was reacted with $VOCl_3$ /toluene in a flow of N_2 at 75°C for 5 hrs. The resulting solid was filtered and dried at 110°C for 4 h and then calcined at 400°C for 4 hrs. Various catalysts containing V_2O_5 were obtained by adjusting the reaction parameter: 5.1, 8.0, 9.0, 10.5, 11.9, 15.5, 22.0 and 31.2 wt %.

In this preparation method, vanadium can be directly bonded at the support surface through the reaction with present OH groups. This mechanism is corresponding with FTIR spectroscopic results (Figure 1).

The surface areas of the support and the catalysts were investigated by BET method and their V_2O_5 content was determined by EDX method. The mechanism of the preparation reaction is as in the following:



The pyridine adsorption

The FTIR measurements were carried out with a Nicolet 5XD FTIR Spectrometer. The measurement apparatus consisted of a conventional closed-circulation system equipped with two IR cells, a gas-dosing volume in the circulation loop and a pressure gauge. After the disc $\{V_2O_5/TiO_2(A)\}$ was placed in the IR cell, the temperature was slowly increased from room temperature up to 400°C *in vacuo* and kept at that temperature for 10 hrs. Then, the disc was heated in the presence of oxygen (ca. 15 torr) at 400°C for 2 hrs. which was then treated with pyridine vapour at 25°C for 15 min. The unadsorbed surplus pyridine vapour was removed under vacuum and the IR-spectroscopic measurements were carried out before and after the treatment of the sample with pyridine at room temperature.

Results and Discussion

IR Absorption bands of HO-groups on the support material, $TiO_2(A)$, and $V_2O_5/TiO_2(A)$ catalysts in the region $3400\text{--}4000\text{ cm}^{-1}$ are illustrated in Figure 1. In the IR-spectrum of $TiO_2(A)$, the characteristic bands of HO-groups are at $3640, 3674, 3688$ and 3725 cm^{-1} ; for $V_2O_5/TiO_2(A)$ catalysts in the same region only the band at 3640 cm^{-1} is observed. The absorbance of this band at 3640 cm^{-1} decreased with increasing V_2O_5 content and when multilayer of V_2O_5 was reached it disappeared completely. The Decreasing of the absorbance at 3640 cm^{-1} and the other bands of HO-groups with increasing V_2O_5 content shows that active component V_2O_5 is bonded to the support $TiO_2(A)$ via HO-groups.

The IR spectra of $TiO_2(A)$ and $V_2O_5/TiO_2(A)$ in the $1800-2200\text{ cm}^{-1}$ region are given in Figure 2. $V_2O_5/TiO_2(A)$ catalysts show a V=O overtone vibrational band at 2040 cm^{-1} while $TiO_2(A)$ does not have any absorption bands in the same region. This peak was also observed between $2035-2045\text{ cm}^{-1}$ in previous works^{5,6}. This means that $92\text{ m}^2\text{ g}^{-1}$ BET surface area of the support $TiO_2(A)$ is covered by a monolayer of V_2O_5 molecules when $n_{th} = 1$. In the region of $1800-2200\text{ cm}^{-1}$ on IR spectra of vanadium oxide multilayer $V_2O_5/TiO_2(A)$ catalysts, the second bands of bulk phase was observed at 1975 cm^{-1} . These bands are characteristic for V=O as explained in the literature^{5,6}.

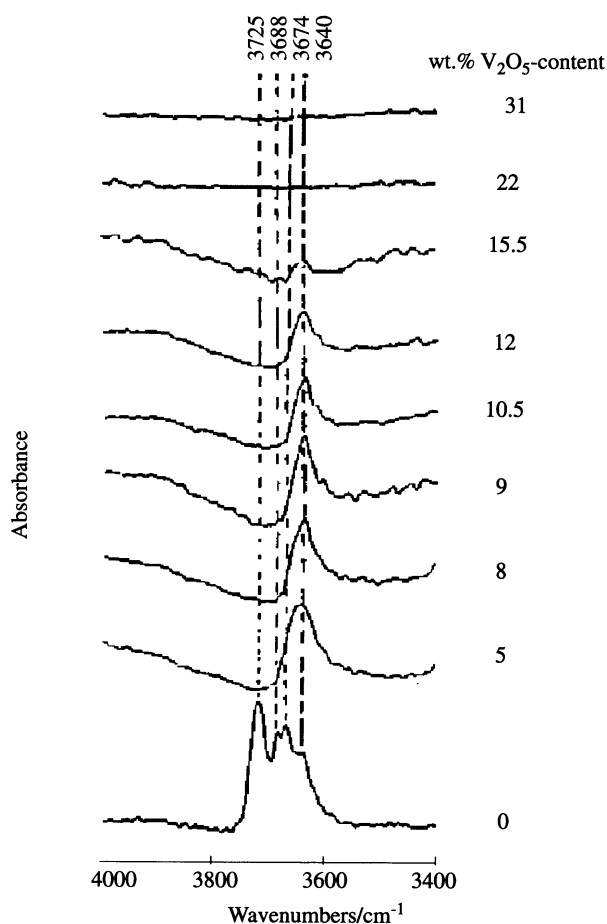


Figure 1. IR-spectra of HO-Groups of $TiO_2(A)$ and the $V_2O_5/TiO_2(A)$ catalysts in the region $3400-4000\text{ cm}^{-1}$

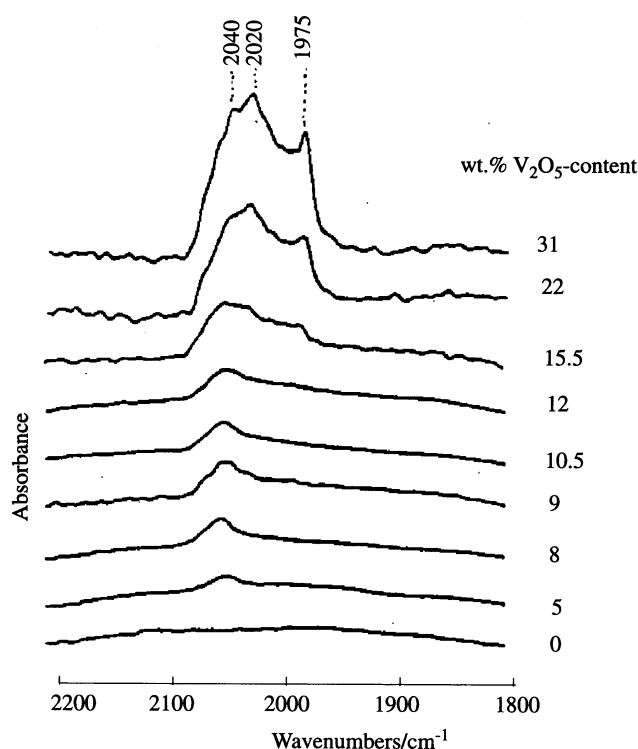


Figure 2. Overtone vibrational bands of V=O of $TiO_2(A)$ and the $V_2O_5/TiO_2(A)$ catalysts

The IR-spectra of pyridine adsorption on the catalyst surfaces are shown in Figure 3. After pyridine adsorption on the disc of $TiO_2(A)$ support material and the disc of $V_2O_5/TiO_2(A)$ catalysts, the IR-spectrum of $TiO_2(A)$ shows only the Lewis acid site absorption bands at $1448, 1488, 1575, 1608\text{ cm}^{-1}$, while the IR spectrum of $V_2O_5/TiO_2(A)$ shows both the Lewis acid site bands and Brönsted acid site band at 1538 cm^{-1} .

The bands of Brönsted acid sites (1538 cm^{-1}) and Lewis acid sites (1448 cm^{-1}) are characteristic for pyridine adsorption on the catalyst surface^{7,8}. The areas under the absorption curves of the bands of these acid sites are taken as measures of the number of acid sites on $V_2O_5/TiO_2(A)$ catalysts surface⁹. It was seen that the number of Lewis acid sites (NLAS) continuously decrease with increasing V_2O_5 content (Figure 4). This decrease of the Lewis acid sites is due to coverage of the acid sites of the support material with increasing amount of V_2O_5 . On the other hand, the number of Brönsted acid sites (NBAS) increase

with increasing V_2O_5 content and reach a maximum when the surface of the support material is covered by a monolayer of V_2O_5 ($n_{th}=1$) and then decrease. It can be concluded that the decrease in the number of the Brönsted acid sites up $n_{th} > 1$ is due to the decrease of the BET surface area of the catalyst.

As proposed by Basila and Katner¹⁰, the B_{Py}/L_{Py} ratio was calculated from the equation;

$$\frac{B_{Py}}{L_{Py}} = \frac{[A_{1490} - C \cdot A_{1450}]}{6.0 \cdot C \cdot A_{1450}}$$

A: Absorbance

$C = \varepsilon_{1490} / \varepsilon_{1450}$

B_{Py} : the number of Brönsted acid sites (NBAS)·

L_{Py} : the number of Lewis acid sites (NLAS)

and it is illustrated in Figure 5 as a function of V_2O_5 content. The ratio of the number of Brönsted acid sites to the number of Lewis acid sites [B_{Py}/L_{Py}] or [NBAS/NLAS] increase with increasing V_2O_5 content and reaches a maximum at $n_{th} = 1$ which is then decreases with increasing V_2O_5 content.

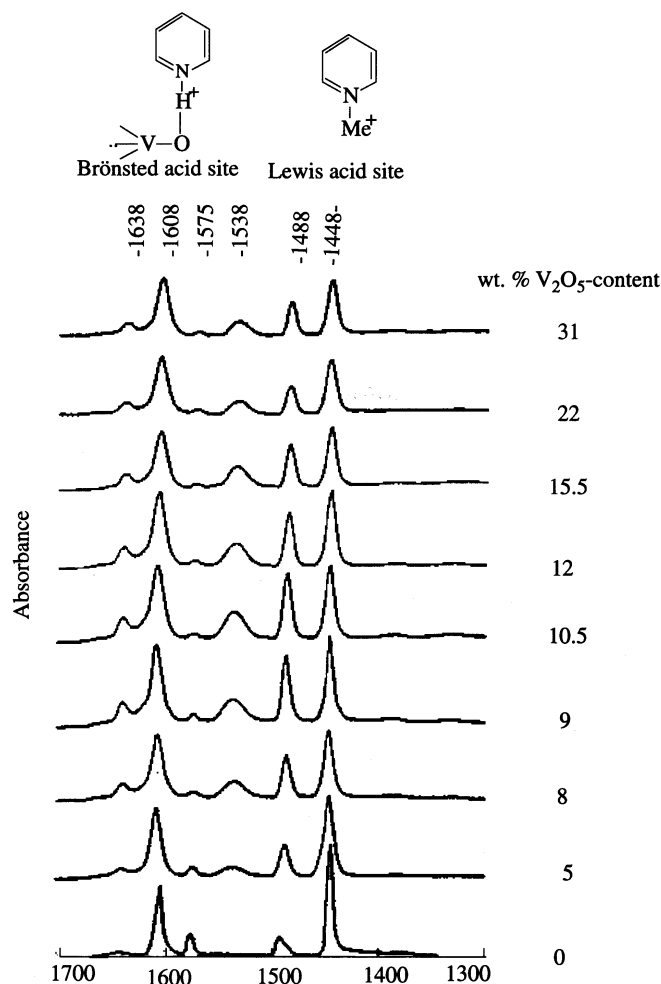


Figure 3. IR spectra of pyridine on $TiO_2(A)$ and $V_2O_5/TiO_2(A)$ catalysts in the region $1300-1700\text{ cm}^{-1}$

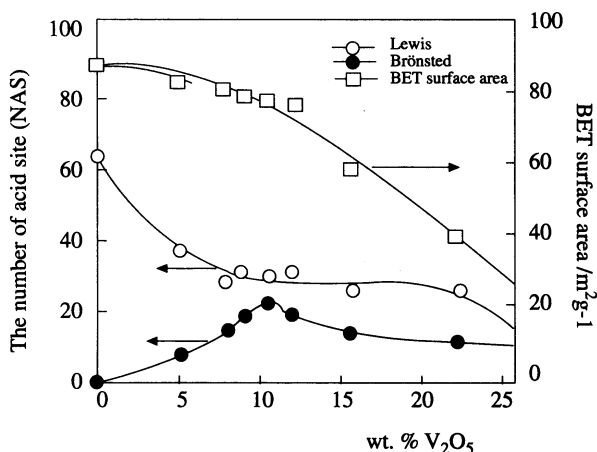


Figure 4. Variation of the number Lewis and Brønsted acid sites on $V_2O_5/TiO_2(A)$ catalysts with V_2O_5 content and with BET surface area at ambient temperature

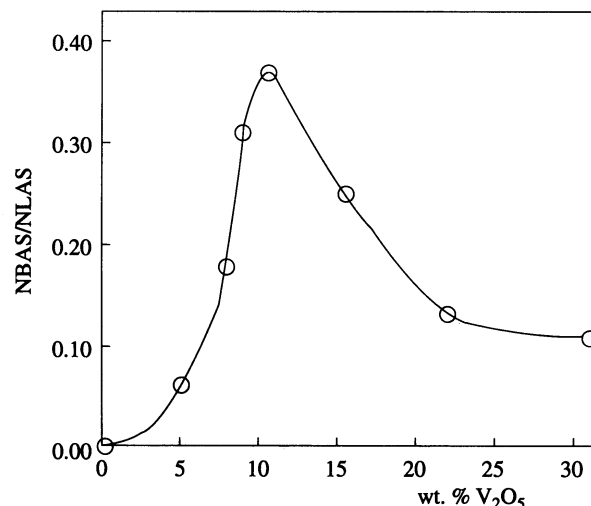


Figure 5. Variation of the ratio of the number Brønsted acid sites (NBAS) to the number Lewis acid sites (NLAS) on $V_2O_5/TiO_2(A)$ catalysts with V_2O_5 content

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