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FT-IR STUDY OF THE ADSORPTION OF PROPANE AND PROPENE
ON $V_2O_5 / \gamma-Al_2O_3$ CATALYST

Key words: $V_2O_5 / \gamma-Al_2O_3$ Catalyst, Propane, Propene Adsorption, FTIR

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ABSTRACT

It has been observed on the oxidized $V_2O_5 / \gamma-Al_2O_3$ that C_3H_6 form alkoxides which were converted to acetone during the desorption of adsorbate phase at 373 K. C_3H_8 may form π -complexes on the reduced form of the same catalyst. However, the intensities of the bands in the adsorption of C_3H_8 were very weak as compared with the case of C_3H_6 adsorption. Therefore, it was not reasonable to assign these bands clearly as any of the surface type species.

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INTRODUCTION

The elucidation of the mechanism of heterogeneous catalysis requires the knowledge of the nature of intermediates responsible for the formation of the products. In general, the IR spectroscopic method is one of the most powerful techniques for the study of chemisorbed species on a catalyst surface.

The study of the IR spectra of surface complexes of propene on various oxide catalyst has already been investigated.⁽¹⁻⁹⁾ On the other hand, adsorption of propane on the oxide catalysts has not been studied in details yet.

It has been shown that propene forms an alcoholate type complex which is converted to acetone that gives enolate-like compounds at elevated temperatures on the oxidized surface of $V_2O_5/\gamma-Al_2O_3$ catalyst. However, on the reduced catalyst which contains mainly V^{4+} and V^{3+} ions, C_3H_6 forms π -complexes; at elevated temperatures and in the presence of O_2 , these complexes are converted to acrylate-like surface compounds that are stabilized on the $\gamma-Al_2O_3$.^(3,5,6,9)

The aim of this work is to elucidate the nature of adsorbed propene and especially propane forms on the surface of $V_2O_5 / \gamma-Al_2O_3$ catalyst.

EXPERIMENTAL

For alumina-supported vanadium oxide catalyst, an appropriate amounts of $\gamma-Al_2O_3$ (Ventron, No. 89375) powder

was added to an aqueous alkali solution of ammonium vanadate, NH_4VO_3 (Merck, 99%). The suspension was evaporated with stirring to dryness. The resulting product was calcined at 823 K for 6 h. This solid was ground into a fine powder and used as a catalyst.

The BET surface area was measured by nitrogen adsorption at 77 K in Ströhlein Areameter. The actual composition of the catalyst was determined by energy dispersive X-ray spectrometer (EDX) after the catalyst was pressed onto inert boric acid matrix. X-ray powder diffraction patterns were performed on a Philips diffractometer using $\text{Cu K}\alpha$ radiation.

For adsorption studies, the catalyst powder was pressed into self-supporting disc of an appropriate thickness and activated by recalcination and evacuation generally at 773 K into the IR cell, connected to a vacuum dosing system. The IR spectra were recorded "in situ" in a conventional vacuum system by Nicolet 60SX Fourier Transform Spectrometer, using variable-temperature quartz cell which was constructed accordingly in Ref.10. In order to obtain the adsorbate spectra, FT-IR spectrum of the unloaded catalyst sample which was recorded as reference spectrum, was subtracted from the obtained spectrum after the adsorption of the gases.

RESULTS AND DISCUSSIONS

The BET surface area and the V_2O_5 content of catalyst were $200 \text{ m}^2/\text{g}$ and 10% V_2O_5 on $\gamma\text{-Al}_2\text{O}_3$ respectively.

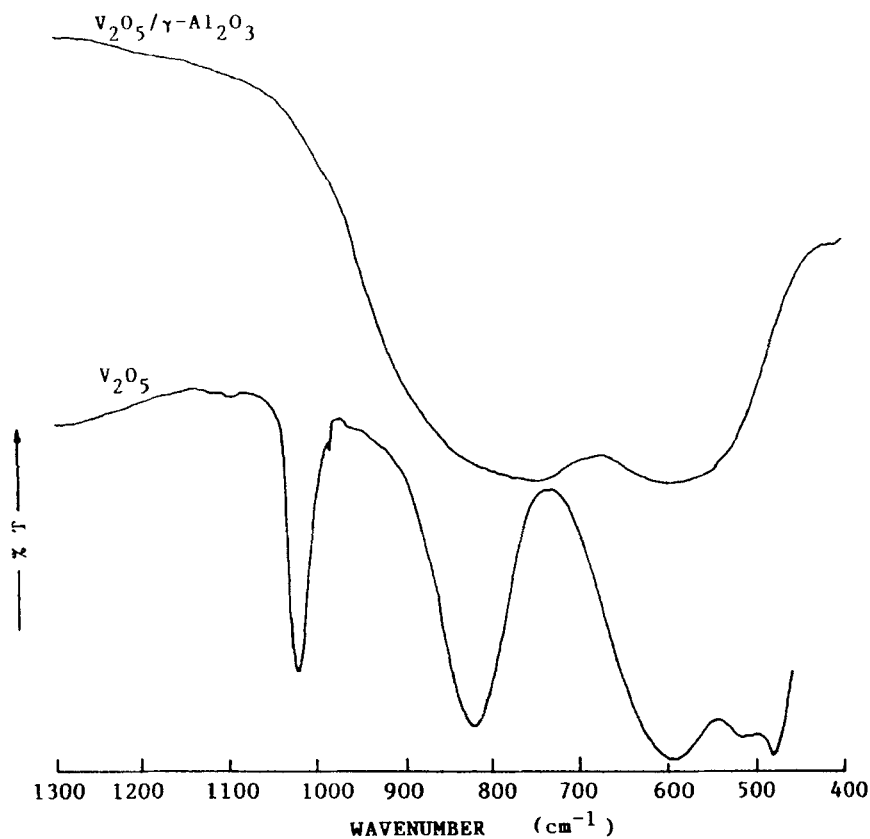


Figure 1. FTIR Spectra of V_2O_5 and $V_2O_5/\gamma-Al_2O_3$ in KBr

The FTIR spectra of pure V_2O_5 and the catalyst in KBr in the region 400 to 1300 cm^{-1} were shown in Fig.1.

Inspection of these spectra showed that a sharp band at 1020 cm^{-1} due to $V=O$ stretching vibration in pure V_2O_5 was absent in the spectrum of the catalyst. The catalyst exhibits only the bands of $\gamma-Al_2O_3$. Results of X-ray diff-

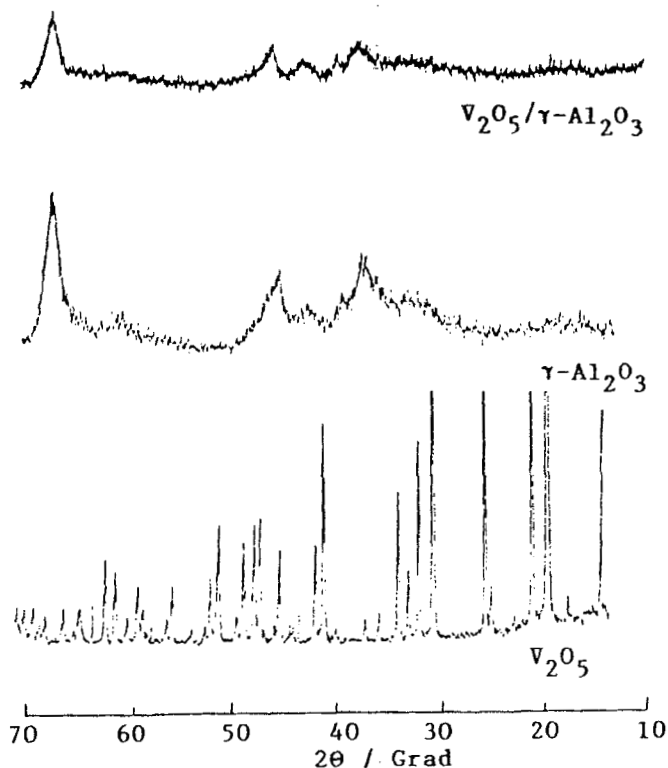


Figure 2. X-Ray Powder Diffraction Patterns of V_2O_5 , $\gamma-Al_2O_3$ and $V_2O_5 / \gamma-Al_2O_3$

raction for V_2O_5 , $\gamma-Al_2O_3$ and the catalyst were presented in Fig.2.

X-ray powder diffraction patterns of the catalyst showed only $\gamma-Al_2O_3$. No V_2O_5 peaks were detected in the catalyst.

The adsorption of propene at 298 K on the oxidized nonhydrated catalyst $V_2O_5 / \gamma-Al_2O_3$ (treated 2h at 723 K in 60 Torr O_2 and evacuated 1h at the same temperature) provided adsorption bands after first contact (Fig.3a) at

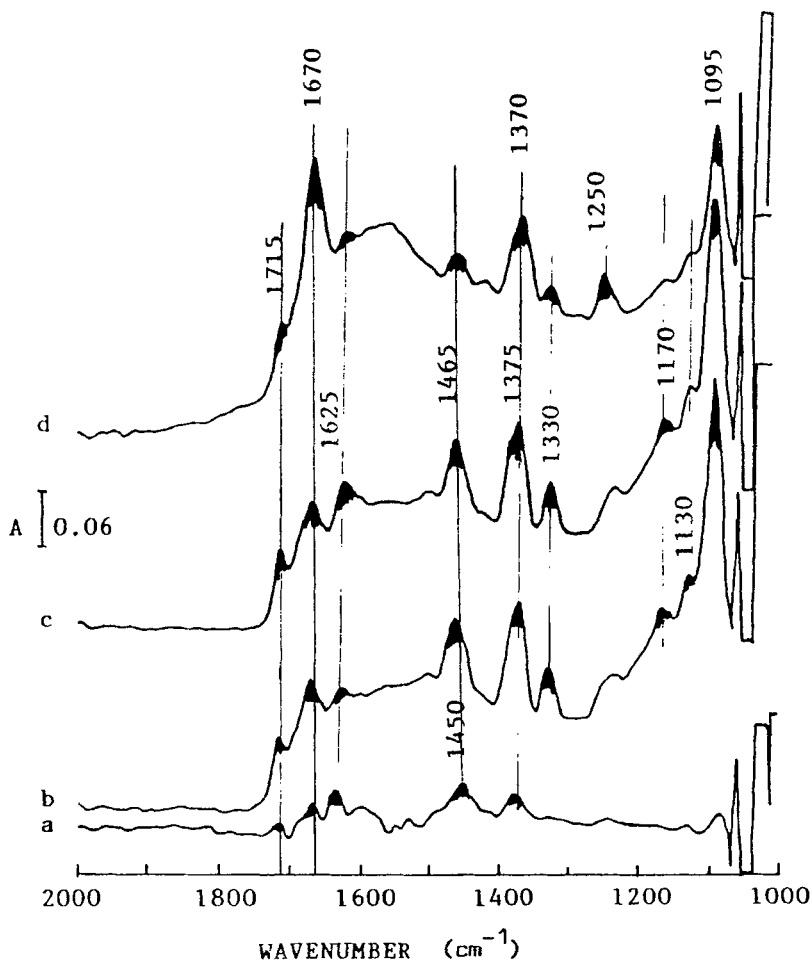


Figure 3. FTIR Spectra of C₃H₆ Adsorbed on V₂O₅ / γ-Al₂O₃
 a) first contact b) 24 h c) after evacuation at 298 K d) after evacuation at 373 K

1095, 1375, 1450, 1625, 1670, 1715 cm^{-1} and a wide unresolved band in the region of 1500 - 1670 cm^{-1} in the IR spectrum.

After 24h from the beginning of the adsorption of propene, led to the increase in the band intensities and also the appearance of the bands at 1330, 1250, 1170 and 1130 cm^{-1} (Fig. 3b). Evacuation of the adsorbed phase at 298 K in a short time interval had particularly no effect on the intensity of the bands but reduced the intensity of the 1670 cm^{-1} band (Fig. 3c). The absence of absorption bands in the spectra of adsorbed propene in the region of (C=C) which is at 1638 cm^{-1} in the spectrum of free propene, indicates that the chemisorption of propene occurs with the opening of the double bond. The absorption band at 1095 cm^{-1} which is not observed in the gas phase spectrum of propene, is typical for C-O stretching vibrations in the surface compounds of Me - O - R type. This indicates the formation of alcoholate type complex on the catalyst surface. It is also well known that ketones are best characterized by the strong C=O stretching frequency absorption near 1715 cm^{-1} . Ketone carbonyls between saturated hydrocarbon groups absorb strongly at 1725-1705 cm^{-1} in most cases. A CH_3 group next to the carbonyl has a strong band due to symmetric CH_3 deformation at 1370-1350 cm^{-1} , which is lower and more intense than alkane CH_3 group absorption. A CH_2 group next to carbonyl has a

strong band due to CH_2 deformation at $1440\text{--}1405\text{ cm}^{-1}$ which was absent in this case. The asymmetric C - C - C stretching vibration gives rise to a medium intensity band at $1230\text{--}1100\text{ cm}^{-1}$. This band was here at 1170 cm^{-1} . However, at higher temperatures of evacuation (Fig.3d), the concentration of alcoholate type complex decreases as indicated by the decrease in the intensity of the bands at 1095 , 1330 and 1465 cm^{-1} . On the other hand, an increase was observed in the intensity of the bands at 1250 and 1670 cm^{-1} . These last two bands, according to references 6,9,11 may be characterized the carbonyl stretching vibration (1675 cm^{-1}) and stretching vibration of C - C (1250 cm^{-1}) which indicated the conversion of alcoholate type complex to acetone. The unresolved absorption in the $1500\text{--}1670\text{ cm}^{-1}$ region may be related to the formation of acetone and the appearance of products of its dissociation on the dehydrated oxidized surface of the catalyst.

However, the band at 1625 cm^{-1} might also be characterized as the C=C stretching frequency absorption. In general, the absorption at 1640 cm^{-1} characterizes a π -complex, hence fixed propene is not subjected to destructive fixation. The formation of this complex is the first step for the selective oxidation of propene via a surface allyl. This band was also absent in the studies of Davydov et al.(6,9)

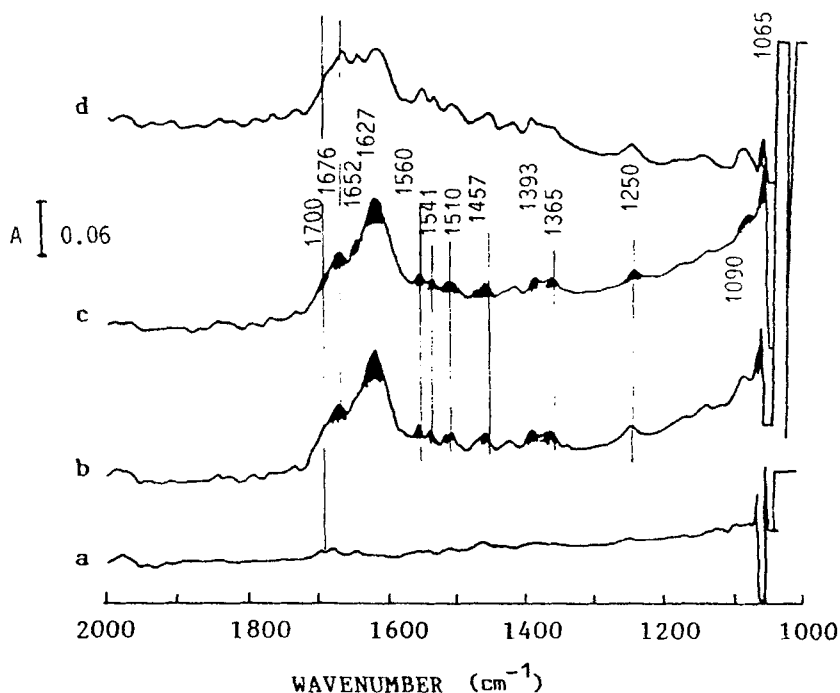


Figure 4. FTIR Spectra of C_3H_8 Adsorbed on $V_2O_5 / \gamma-Al_2O_3$
a) first contact b) 24 h c) after evacuation at 298 K d) after evacuation at 373 K

The C=C vibration interacts to some extent with $=CH_2$ deformation vibration and to some extent with the single bond stretching vibration. The CH_2 scissors deformation of the vinyl and vinylidene groups give rise to a medium intensity band in the infrared spectra near 1415 cm^{-1} . This band was also absent in this case. Therefore, it was difficult to say the formation of such a π -complex. This band may also be due to $\delta(OH)$ bending vibration of H_2O .

We have studied adsorption of propane at 298 K on the same catalyst at a pressure of about 3 Torr after propene adsorption without any oxidation procedure. The obtained adsorbate spectra was shown in Fig.4.

After exposing the catalyst to propane, any attributable absorption band could be seen at first (Fig.4a). This implied that the adsorption of propane on the surface of the catalyst was weaker as compared with propene as far as the intensity of the bands concern. After 24 h (Fig.4b), the bands at 1065, 1090, 1250, 1365, 1393, 1457, 1510, 1541, 1560, 1627 and 1676 cm^{-1} could be seen. However only the bands at 1676, 1627 and 1065 cm^{-1} were stronger than the bands in the region of 1300-1600 cm^{-1} . Different types of surface compounds such as a π -complex (bands at 1365, 1457 and 1627 cm^{-1}), formation of an alcoholate type complex transforming into acetone (bands at 1090, 1250 and 1676 cm^{-1}) might be present on the surface of the catalyst. There was not any difference between Fig.4b and Fig.4c. However, pumpdown to remove the gas phase at 373 K leaded to practically a decrease in the intensity of the band at 1627 cm^{-1} , and also appearance of the band at 1652 cm^{-1} which was shoulder before this stage. Meanwhile, any other practical change in the spectrum had been observed (Fig.4d). It has been stated that at a pressure of about 2 Torr (low coverage) propane also adsorbs only in the form of formate species. On the other hand, at increased pres-

tures (high degree of coverage), formation of carboxylate structures along with formate species was observed on the surface of CuO/MgO catalyst.⁽¹³⁾ The assignment of the bands around 1650 cm^{-1} is rather difficult. This is the region of the double bond stretch vibration, but it is also assigned to some carbonate structures. The bands at 1360 and $1580\text{--}1590\text{ cm}^{-1}$ were assigned as symmetric and antisymmetric vibrations of a COO^- group in a formate type structure, HCOO^- . While adsorption bands at 1450 and $1540\text{--}1560\text{ cm}^{-1}$ may be due to ν_s and ν_{as} vibrations of a COO^- in an acetate type of complex, CH_3COO^- .⁽¹³⁾

Thus, we could conclude tentatively that on the oxidized surface of $\text{V}_2\text{O}_5 / \gamma\text{-Al}_2\text{O}_3$ catalyst, in the adsorption of propene, even at 298 K , a proton is transferred to propene forming a surface compound of the alcoholate type; with the passage of time or with an increase in temperature, this complex is converted to acetone. Similar results were also obtained in the study of the IR spectra of propene adsorbed on the oxidized surface of the V_2O_5 catalysts by Davydov et al.^(3,5,6,9,13)

However, in this study, the predominant form of C_3H_6 adsorption at low temperature might be the formation of π -complexes. One of the most interesting problem here is the elucidation of the paths of formation and also conversion of the surface π -complexes.

Further work to attempt to clarify the nature of adsorbed propane forms which appear on the surface of vanadium based catalysts is in progress.

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