CHARACTERIZATION OF SUPPORTED METAL OXIDES BY LASER RAMAN SPECTROSCOPY: SUPPORTED VANADIUM OXIDE ON $\text{Al}_2\text{O}_3$ AND $\text{TiO}_2$

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ABSTRACT

The interaction of supported vanadium oxide with $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ substrates is examined with Raman spectroscopy. The Raman spectra of the supported vanadium oxide reveal that the strong interaction of the vanadium oxide with the $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ supports results in the formation of an atomically dispersed surface vanadium oxide phase as well as supported crystalline $\text{V}_2\text{O}_5$. The relative concentrations of the atomically dispersed surface vanadium oxide and crystalline $\text{V}_2\text{O}_5$ depend on the vanadium oxide loading and the surface area of the oxide support.

INTRODUCTION

Supported metal oxides are formed when one metal oxide phase is dispersed on a second metal oxide substrate. The dispersed supported metal oxide phase can simultaneously possess several different molecular states. The multiple molecular states that can simultaneously be present in the supported metal oxide phase have acted as a source of confusion and hampered progress in the understanding of supported metal oxide catalysts. This confusion has resulted primarily because of the lack of applicable characterization techniques capable of discriminating between these different molecular states. Conventional catalyst characterization techniques provide general information concerning the physical characteristics of the supported metal oxide phase, but they are not adequate to discriminate between the different molecular states that are simultaneously present [1]. In the past few years, however, characterization studies of supported metal oxides have shown that the different molecular states in the supported metal oxide phase can be discriminated with the use of laser Raman spectroscopy [2]. This technique can discriminate between the different molecular states of the supported metal oxides because each state possesses a unique vibrational spectrum that is related to its structure. Therefore, Raman spectroscopy provides direct information about the structure of each state as well as a method of discriminating between the various states. In the present investigation we report on the Raman spectroscopy of supported vanadium oxide on $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ supports. The influence of the oxide supports upon the...
structural nature of the supported vanadium oxide phases and their catalytic properties will be discussed.

EXPERIMENTAL

The supported metal oxide catalysts were prepared by the incipient-wetness impregnation method. The oxide supports consist of $\gamma$-Al$_2$O$_3$ (Harshaw, 180 m$^2$/g) and TiO$_2$ (Degussa P-25, anatase/rutile, 55 m$^2$/g). The V$_2$O$_5$/TiO$_2$ samples were made with VO(OC$_2$H$_5$)$_3$, in ethanol, dried at room temperature for 16 hrs, dried at 110-120°C for 16 hrs, and calcined at 450°C for 2 hrs. The V$_2$O$_5$/Al$_2$O$_3$ samples were made with VO(OC$_3$H$_7$)$_3$, in methanol, dried at room temperature for 16 hrs, dried at 110-120°C for 16 hrs, and calcined at 450°C for 16 hrs. Several of the above samples were further calcined at higher temperatures in order to examine the influence of calcination temperature upon the supported vanadium oxide systems.

The Raman spectra were obtained with a Spectra-Physics Ar$^+$ laser delivering 1-100 mW of incident radiation measured at the sample, where the exciting line was typically 514.5 nm. The scattered radiation was then directed into a Spex Triplemate Spectrometer (Model 1877) coupled to a Princeton Applied Research OMA III optical multichannel analyzer (Model 1463) with an intensified photodiode array cooled thermo-electrically to -30°C. The Raman spectra were recorded using an OMA III dedicated computer and software. All Raman spectra were obtained at room temperature and under ambient conditions. Additional details concerning the optical arrangement of the laser Raman apparatus can be found elsewhere [2].

RESULTS AND DISCUSSION

The interaction of vanadium oxide with the Al$_2$O$_3$ support is reflected in the Raman spectra presented in Figure 1. The nature of the supported vanadium oxide phases is determined by comparison of the Raman spectra of the supported vanadium oxide catalysts with spectra of vanadium oxide reference compounds [3-8]. The 3-20 wt% V$_2$O$_5$/Al$_2$O$_3$ catalysts do not contain the Raman features of either crystalline V$_2$O$_5$ (major bands at 1000, 703, 525, and 150 cm$^{-1}$) or AlVO$_4$ (major bands at 1017, 988, 949, 899, 510, 391, 319, 279, and 133 cm$^{-1}$), but possess weak and broad Raman bands characteristic of an atomically dispersed surface vanadate species. The surface vanadate species possesses bands in the 900-1000 cm$^{-1}$ region which are characteristic of V=O symmetric stretching modes and bands at $\approx$500 and 220 cm$^{-1}$ which are characteristic of V-O-V linkages. The Raman spectra of the 22-30% V$_2$O$_5$/Al$_2$O$_3$ catalysts, however, are composed of the Raman features diagnostic of crystalline V$_2$O$_5$ which overshadow the weaker Raman features of the atomically dispersed surface vanadate phase. Thus, a monolayer of the surface vanadate species on alumina corresponds to $\approx$20% V$_2$O$_5$/Al$_2$O$_3$ for this system.
Figure 1. Raman spectra for $V_2O_5/Al_2O_3$ catalysts at sub-monolayer coverages: (a) 3% $V_2O_5/Al_2O_3$, (b) 5% $V_2O_5/Al_2O_3$, (c) 10% $V_2O_5/Al_2O_3$, (d) 20% $V_2O_5/Al_2O_3$; and at coverages exceeding the monolayer: (e) 22% $V_2O_5/Al_2O_3$, (f) 30% $V_2O_5/Al_2O_3$.

Figure 2. Raman spectra for $V_2O_5/TiO_2$ (Degussa) catalysts at sub-monolayer coverages: 1%, 1.8%, 2.5%, 4%, and 6% $V_2O_5/TiO_2$; and above monolayer coverage: 8% $V_2O_5/TiO_2$. 
The Raman spectra for the supported vanadium oxide on TiO₂ catalysts are presented in Figure 2. In general, the very strong TiO₂ Raman features below 700 cm⁻¹ prevent the acquisition of Raman spectra in this region for supported metal oxides on TiO₂. Furthermore, the TiO₂ support possesses a weak band at ≈796 cm⁻¹ which arises from the first overtone of its very strong band at 398 cm⁻¹. The 1-6% V₂O₅/TiO₂ catalysts do not exhibit the Raman features of crystalline V₂O₅, but possess weak and broad Raman bands characteristic of an atomically dispersed surface vanadate species. The surface vanadate species possesses bands in the 900-1000 cm⁻¹ region which are characteristic of V=O symmetric stretching modes. The intensity of the weak TiO₂ band at ≈796 cm⁻¹ decreases as the vanadium oxide coverage is increased because of the dramatic increase in the absorptivity coefficient (sample color) of the sample in the visible region of the spectrum (i.e., a fraction of the Raman signal is absorbed by the sample matrix). The Raman spectrum of the 8% V₂O₅/TiO₂ catalyst is dominated by the band of crystalline V₂O₅ at 1000 cm⁻¹ and overshadows the weaker Raman features of the atomically dispersed surface vanadate phase. Thus, a monolayer of the surface vanadate on titania corresponds to ≈7% V₂O₅/TiO₂ for this system.

### TABLE I

<table>
<thead>
<tr>
<th>Sample</th>
<th>450°C</th>
<th>700°C</th>
<th>850°C</th>
<th>950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>56 m²/g</td>
<td>31 m²/g</td>
<td>12 m²/g</td>
<td>-</td>
</tr>
<tr>
<td>5% V₂O₅/TiO₂</td>
<td>46 m²/g</td>
<td>17 m²/g</td>
<td>5 m²/g</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>180 m²/g</td>
<td>-</td>
<td>-</td>
<td>94 m²/g</td>
</tr>
<tr>
<td>5% V₂O₅/Al₂O₃</td>
<td>178 m²/g</td>
<td>-</td>
<td>-</td>
<td>3 m²/g</td>
</tr>
</tbody>
</table>

* TiO₂ samples calcined for 2 hrs; Al₂O₃ samples calcined for 16 hrs.

The influence of elevated calcination temperatures upon the V₂O₅/Al₂O₃ and V₂O₅/TiO₂ systems was also investigated [8,9]. Both of these systems exhibited very dramatic decreases in surface area upon calcination between 700-950°C, and the corresponding surface areas are shown in Table I. Note that the presence of the supported vanadium oxide phase dramatically accelerates the loss in surface area of both the Al₂O₃ and TiO₂ supports. The significant loss in surface area of the oxide
supports serves to increase the surface density of surface vanadium oxide and transforms the surface vanadate species to crystalline V₂O₅. The supported crystalline V₂O₅ is stable on the Al₂O₃ support and does not undergo any solid state reactions at elevated temperatures. The supported crystalline V₂O₅, however, is not stable on the TiO₂ support and does undergo a solid state reaction with the titania support to form crystalline VₓTi₁₋ₓO₂ (rutile) after reduction of the vanadium from the +5 to the +4 oxidation state.

Many recent studies have shown supported V₂O₅ catalysts to be superior catalysts to unsupported V₂O₅ catalysts for the selective oxidation of many hydrocarbons [7,8,10-17]. Furthermore, the surface vanadate species were found to be the active sites for these partial oxidation reactions, and to possess a higher activity and selectivity than crystalline V₂O₅ for many hydrocarbon oxidation reactions. The oxide supports must be covered by a complete monolayer of the surface vanadate species since exposed support sites lead to combustion of the partial oxidation products. Moderate amounts of crystalline V₂O₅ do not significantly affect the catalytic performance of supported vanadium oxide catalysts because of the low effective surface area and poor catalytic activity of this phase. The unique properties of the surface vanadate monolayer on oxide supports are related to the specific nature of the vanadia/oxide support interactions.

CONCLUSION

The interaction of supported vanadium oxide with Al₂O₃ and TiO₂ supports was investigated with Raman spectroscopy. Both the alumina and titania supports exhibit very strong capacities for forming atomically dispersed surface vanadium oxide phases. The supported vanadium oxide phase is found to influence the surface area of the oxide support upon calcination.

REFERENCES

2. I.E. Wachs, F.D. Hardcastle, and S.S. Chan, Spectrosc. 1(8) 30 (1986).


