CHARACTERIZATION OF SUPPORTED METAL OXIDES BY LASER RAMAN
SPECTROSCOPY: SUPPORTED VANADIUM OXIDE ON $Al_2O_3$ AND $TiO_2$

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ABSTRACT

The interaction of supported vanadium oxide with $Al_2O_3$ and
$TiO_2$ 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 $Al_2O_3$ and $TiO_2$
supports results in the formation of an atomically dispersed
surface vanadium oxide phase as well as supported crystalline
$V_2O_5$. The relative concentrations of the atomically dispersed
surface vanadium oxide and crystalline $V_2O_5$ 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 $Al_2O_3$ and $TiO_2$
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 $\gamma$-$Al_2O_3$ (Harshaw, 180 $m^2$/g) and $TiO_2$ (Degussa P-25, anatase/rutile$\approx$2, 55 $m^2$/g). The $V_2O_5$/$TiO_2$ samples were made with $VO(OC_2H_5)_3$ 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 $V_2O_5$/$Al_2O_3$ samples were made with $VO(OC_3H_7)_3$ 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 $Al_2O_3$ 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% $V_2O_5$/$Al_2O_3$ catalysts do not contain the Raman features of either crystalline $V_2O_5$ (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 charateristic of V-O-V linkages. The Raman spectra of the 22-30% $V_2O_5$/$Al_2O_3$ catalysts, however, are composed of the Raman features diagnostic of crystalline $V_2O_5$ 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% $V_2O_5$/$Al_2O_3$ for this system.
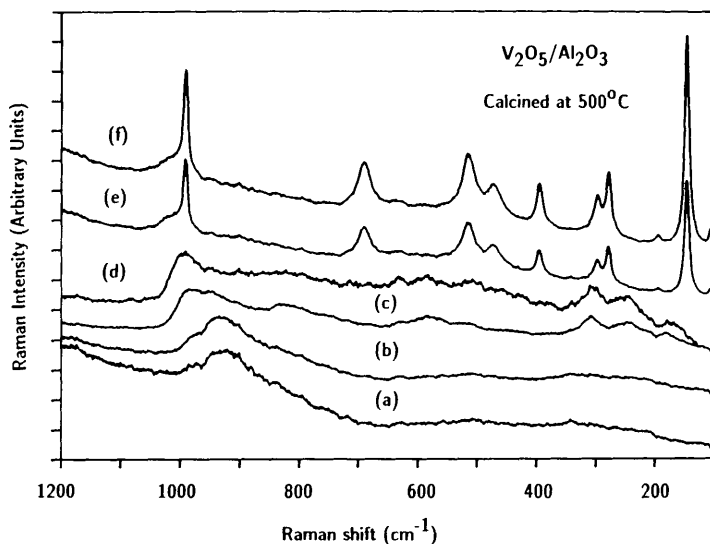
*Figure 1. Raman spectra for $V_2O_5/Al_2O_3$ catalysts at sub-monolayer coverages: (a) 3% $V_2O_5/Al_2O_3$, (b) 5% $V_2O_5/Al_2O_3$, (c) 10% $V_2O_5/Al_2O_3$, (d) 20% $V_2O_5/Al_2O_3$; and at coverages exceeding the monolayer: (e) 22% $V_2O_5/Al_2O_3$, (f) 30% $V_2O_5/Al_2O_3$.*
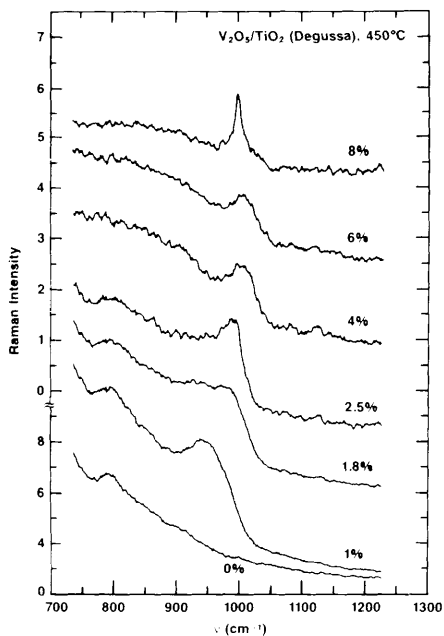


*Figure 2. Raman spectra for $V_2O_5/TiO_2$ (Degussa) catalysts at sub-monolayer coverages: 1%, 1.8%, 2.5%, 4%, and 6% $V_2O_5/TiO_2$; and above monolayer coverage: 8% $V_2O_5/TiO_2$.*

The Raman spectra for the supported vanadium oxide on $TiO_2$ catalysts are presented in Figure 2. In general, the very strong $TiO_2$ Raman features below 700 $cm^{-1}$ prevent the acquisition of Raman spectra in this region for supported metal oxides on $TiO_2$. Furthermore, the $TiO_2$ support possesses a weak band at $\approx$796 $cm^{-1}$ which arises from the first overtone of its very strong band at 398 $cm^{-1}$. The 1-6% $V_2O_5/TiO_2$ catalysts do not exhibit the Raman features of crystalline $V_2O_5$, 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 $TiO_2$ band at $\approx$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% $V_2O_5/TiO_2$ catalyst is dominated by the band of crystalline $V_2O_5$ 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 $\approx$7% $V_2O_5/TiO_2$ for this system.

| TABLE I |
|---|
| Influence of Calcination Temperature on BET Surface Area of Supported Vanadium Oxide on $TiO_2$ and $Al_2O_3$ |

| Sample | Calcination Temperature* | | | |
|---|---|---|---|---|
| | 450°C | 700°C | 850°C | 950°C |
| $TiO_2$ | 56 $m^2$/g | 31 $m^2$/g | 12 $m^2$/g | — |
| 5% $V_2O_5/TiO_2$ | 46 $m^2$/g | 17 $m^2$/g | 5 $m^2$/g | — |
| $Al_2O_3$ | 180 $m^2$/g | — | — | 94 $m^2$/g |
| 5% $V_2O_5/Al_2O_3$ | 178 $m^2$/g | — | — | 3 $m^2$/g |

\* $TiO_2$ samples calcined for 2 hrs; $Al_2O_3$ samples calcined for 16 hrs.

The influence of elevated calcination temperatures upon the $V_2O_5/Al_2O_3$ and $V_2O_5/TiO_2$ 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 $Al_2O_3$ and $TiO_2$ 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 $V_2O_5$. The supported crystalline $V_2O_5$ is stable on the $Al_2O_3$ support and does not undergo any solid state reactions at elevated temperatures. The supported crystalline $V_2O_5$, however, is not stable on the $TiO_2$ support and does undergo a solid state reaction with the titania support to form crystalline $V_xTi_{1-x}O_2$ (rutile) after reduction of the vanadium from the +5 to the +4 oxidation state.

Many recent studies have shown supported $V_2O_5$ catalysts to be superior catalysts to unsupported $V_2O_5$ 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 $V_2O_5$ 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 $V_2O_5$ 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 $Al_2O_3$ and $TiO_2$ 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.

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