The molecular structures and reactivity of $V_2O_5/TiO_2/SiO_2$ catalysts

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A series of $V_2O_5/TiO_2/SiO_2$ catalysts were structurally investigated by *in situ* Raman spectroscopy and chemically probed by methanol oxidation in order to determine the molecular structure-reactivity relationships of the $V_2O_5/TiO_2/SiO_2$ catalysts. Only surface TiO_x species are present on the 3% TiO_2/SiO_2 catalysts, and the surface TiO_x species as well as bulk TiO_2 (anatase) particles coexist on the 40% TiO_2/SiO_2 catalyst. The deposition of 1–3% vanadium oxide onto 3% TiO_2/SiO_2 and 4% vanadium oxide onto 40% TiO_2/SiO_2 forms only a surface vanadium oxide phase. *In situ* Raman studies reveal that the surface vanadium oxide species preferentially exist on the titania sites of the TiO_2/SiO_2 system. The interaction between the surface vanadia and the surface titania overlayer on SiO_2 increases the methanol oxidation reactivity by two orders of magnitude relative to V_2O_5/SiO_2. In the presence of bulk TiO_2 (anatase) particles on the SiO_2 support, the reactivity of the surface vanadia further increases by an order magnitude relative to the catalysts containing only surface titania, and is close to that of surface vanadia on bulk TiO_2. This suggests that the surface VO_x-TiO_2 (bulk) interactions results in a more active site than the surface VO_x-TiO_x-SiO_2 interactions. In addition, the $V_2O_5/TiO_2/SiO_2$ catalysts exhibit high selectivity towards HCHO because redox sites are predominant on the surface of these catalysts with essentially no acid site present.

Keywords: Vanadia; titania; silica; Raman; oxidation

1. Introduction

Recent studies on the $V_2O_5/TiO_2/SiO_2$ catalysts have demonstrated that the presence of TiO_2 on the SiO_2 surface decreases the reduction temperature of the supported vanadia phase, and that these mixed oxide systems exhibit a high reactivity for the selective catalytic reduction (SCR) of NO with NH_3 relative to the V_2O_5/SiO_2 system [1–4]. The use of a SiO_2 support for the V_2O_5/TiO_2 catalysts for the reduction of NO with NH_3 results in a higher surface area, superior sintering resistance, and low cost compared to the TiO_2 support alone [3,5]. In spite of these incentives the $V_2O_5/TiO_2/SiO_2$ catalytic system is not well characterized and understood.

The molecular structures of TiO_2 and SiO_2 supported V_2O_5 catalysts under *in situ* conditions have been extensively characterized with Raman spectroscopy [6–10], infrared spectroscopy (IR) [11], ^{51}V NMR spectroscopy [12], as well as XANES/EXAFS [13]. The dehydrated surface vanadium oxide species on TiO_2 possess a sharp Raman band in the 1027–1031 cm^{-1} region as well as a broad Raman band at ~ 900 cm^{-1}, and the relative intensities of these two bands vary with surface vanadium oxide coverage. The dehydrated V_2O_5/SiO_2 catalyst, however, only possesses a single Raman bound at ~ 1038 cm^{-1}. The dehydrated surface vanadium oxide species which give rise to the sharp Raman bands in the 1027–1038 cm^{-1} region also exhibit IR bands in the 1030–1050 cm^{-1} region. The coincidence of the IR and Raman bands suggests that only one terminal $V=O$ bond is present [11]. The corresponding solid state ^{51}V-NMR shift appears at -640 ppm which is consistent with tetrahedral coordination [12]. From this collective information, the sharp Raman bands in the 1027–1038 cm^{-1} region have been assigned to the isolated vanadate species possessing one terminal $V=O$ bond and three bridging V-O-support bonds [6–14]. The broad Raman band at ~ 900 cm^{-1} has been assigned to polymeric tetrahedral metavanadate species [10,14]. *In situ* XANES/EXAFS studies on SiO_2 supported V_2O_5 catalysts also suggest that the surface vanadium oxide species on SiO_2 possess a mono-oxo tetrahedral vanadate structure [13].

The reactivity of 1% V_2O_5/TiO_2 and 1% V_2O_5/SiO_2 catalysts was probed by the methanol oxidation reaction, and revealed that the turnover number (TON) of the surface vanadium oxide species on TiO_2 (98% HCHO selectivity) is three orders of magnitude higher than the TON on SiO_2 (79% HCHO and 18% CO/CO_2 selectivity) [7]. From the combined structural characterization and the catalytic studies it was proposed that the bridging V-O support bonds rather than the terminal $V=O$ bonds of the surface vanadium oxide species are associated with the active sites during oxidation reactions [7].

Recent Raman, IR, and transmission electron microscopy (TEM) studies reveal that titanium oxide also forms a surface titanium oxide overlayer on SiO_2 [15]. The maximum coverage of the surface titanium oxide species on SiO_2 (Cab-O-Sil, ~ 300 m^2/g) was determined to be $\sim 3\%$ TiO_2/SiO_2. At higher TiO_2 loadings the Raman features of crystalline TiO_2 (anatase) are detected on the SiO_2 surface. The formation of a surface titanium oxide overlayer on SiO_2 was also suggested by Fernandez et al. using XRD, IR, as well as XPS [16], and it was concluded that the coordinatively unsaturated Ti^{3+} sites were present on the SiO_2 surface upon H_2 reduction or high-temperature evacuation. Reichmann and Bell [17] studied high TiO_2 loadings on SiO_2 ($> 7\%$) by XRD, TEM, as well as Raman spectroscopy, and found that crystalline TiO_2(B) formed on SiO_2 at low titanium oxide loadings ($< 10\%$) and crystalline TiO_2 (anatase) was present on SiO_2 at higher titanium oxide loadings. Thus, both surface titania and crystalline TiO_2 are expected on SiO_2 at high TiO_2 loadings.

In comparison to the single component supported metal oxide systems (V_2O_5/TiO_2, V_2O_5/SiO_2, and TiO_2/SiO_2), the mixed oxide system of $V_2O_5/TiO_2/SiO_2$ is not well understood. The molecular structures, location and reactivity of the surface metal oxide species are not known. In this study, the deposition of 1–4% surface vanadium oxide on 3% TiO_2/SiO_2 and 4% TiO_2/SiO_2 were investigated by Raman spectroscopy in order to determine the location and molecular structures of the surface vanadium oxide species as well as the corresponding reactivity which was probed by the methanol oxidation reaction. It was possible to determine the specific interactions of the surface vanadium oxide species with the different phases of the oxide support (surface TiO_x, bulk TiO_2, and SiO_2) from a comparison of the Raman structural information and catalytic behavior of the V_2O_5/TiO_2 system with those of the V_2O_5/TiO_2 and V_2O_5/SiO_2 systems. Thus, such fundamental information allowed us to establish the structure-reactivity relationships of the $V_2O_5/TiO_2/SiO_2$ catalysts.

2. Experimental section

a. MATERIALS AND PREPARATIONS

The 0–3% $V_2O_5/TiO_2/SiO_2$ catalysts were prepared by a two step incipient-wetness impregnation method. The SiO_2 support (Cab-O-Sil, ~ 300 m^2/g) was pretreated at 500°C for 16 hrs under flowing dry air. First, titanium isopropoxide (Aldrich) in a toluene solution was impregnated into the SiO_2 support under a N_2 environment to avoid the decomposition of the air-sensitive precursor. The samples were initially dried at room temperature for 2 hrs, further dried at 120°C for 16 hrs under flowing N_2, and subsequently calcined at 500°C for 16 hrs under flowing dry air to form a supported titanium oxide phase on the SiO_2 support. Subsequently, various concentrations of vanadium isopropoxide (Alfa, 95–99% purity) in a methanol (Fisher, 99.9% purity) solution were impregnated into the TiO_2/SiO_2 support under a nitrogen environment. The samples were dried (at room temperature for 2 hrs and at 120°C for 16 hrs under flowing N_2) and calcined (at 500°C for 1 hr under flowing N_2 and for additional 2 hrs under flowing dry air) to form a supported vanadium oxide phase on the TiO_2/SiO_2 support. The 4% V_2O_5/40% TiO_2/SiO_2 sample was provided by W.R. Grace.

b. RAMAN SPECTROSCOPY

The *in situ* Raman spectroscopy consists of a quartz cell and sample holder, a Spex triplemate spectrometer (Model 1877) coupled to an EG&G intensified photodiode array detector (Model 1420) which were cooled thermoelectrically to −35°C, and an EG&G OMA III Optical Multichannel Analyzer (Model 1463). The samples were excited by the 514.5 nm line of the Ar^+ laser with 10 mW. The laser beam was focused on the sample disk in a right-angle scattering geometry. An ellipsoid mirror collects and reflects the scattered light into the spectrometer's filter stage to reject the elastic scattering. The overall spectral resolution was determined to be better than 2 cm^{-1}. The detailed schematic diagram of the Raman spectrometer is described elsewhere [18].

Prior to the Raman analysis, all samples were calcined at 700°C for 1 hr under flowing dry air in order to diminish the fluorescent background. A 50–100 mg sample disc was held by a stationary U-shaped slot in the quartz cell. The sample was further heated by a cylindrical heating coil surrounding the quartz cell at 400°C for 30 min. Oxygen gas (Linde, 99.9% purity) was introduced into the cell from a manifold at a rate of 50–500 cm^3/min upon dehydration. The *in situ* Raman spectra were recorded after the quartz cell was cooled down to room temperature.

c. CATALYSIS STUDIES

Catalysis studies on the $V_2O_5/TiO_2/SiO_2$ catalysts were performed with the sensitive methanol oxidation reaction in order to determine the relative reactivity of this series of catalysts. The catalytic reactor consisted of a digital flow rate controller (Brooks), a tube furnace (Lindberg), a condenser and methanol reservoir, and an on-line gas chromatograph (HP 5840). A portion of the methanol in the methanol reservoir was constantly evaporated under a controlled temperature and pressure. The evaporated methanol was mixed with the He and O_2 gases whose flow rates were adjusted by the mass flow rate controller. This mixed gas flowed through the condenser maintained at a temperature of 9.6°C. The methanol content was obtained by calculating the partial pressure of methanol at this temperature. The 6.9 : 11.0 : 0.82.1 ratio of the $CH_3OH/O_2/He$ gaseous mixture then flowed to the reactor. The catalysts were placed in the center of a 6 mm OD Pyrex microreactor supported by glass wool, and activated at 400°C by a programmable tube furnace under flowing pure oxygen. The reactor was then cooled down to the reaction temperature (230°C). The effluent gases were analyzed on-line by the gas chromatograph. The gas chromatograph was modified to operate with two thermal conductivity detectors (TCD) and one flame ionization detector (FID), and programmed to perform automatic data acquisition and analysis. The catalytic activity and selectivity were obtained by integrating the peak areas of the products with respect to the reference peak area of methanol. The methanol conversion was kept below 10% to avoid complications due to heat and mass transfer limitations.

3. Results

RAMAN SPECTRA OF THE SUPPORTED TITANIUM OXIDE ON SILICA

The SiO_2 support possesses Raman features at ~ 452 and ~ 803 (siloxane linkages), ~ 605 and ~ 488 (three- and four-fold siloxane rings), ~ 979 (surface silanol groups), and ~ 1050 cm^{-1} (the antisymmetric mode of the Si-O-Si linkages) as shown in fig. 1 [19,20]. Upon the addition of 3% TiO_2 onto the SiO_2 support, a weak and broad Raman band appears under ambient conditions at ~ 960 cm^{-1} which is characteristic of a surface titanium oxide overlayer [15]. The absence of crystalline TiO_2 (anatase) (Raman bands at ~ 640, ~ 520, ~ 399, and ~ 144 cm^{-1}) further confirms the presence of the surface titanium oxide overlayer. Under *in situ* conditions, the Raman features of the dehydrated 3% TiO_2/SiO_2 sample possess very weak perturbations at ~ 788, ~ 920, and ~ 1060 cm^{-1} (see fig. 1). These small perturbations are thought to be related to Ti-O-Si vibrations, but the small Raman cross-section of the surface titania species prevents any detailed structural assignment of the surface titania species.

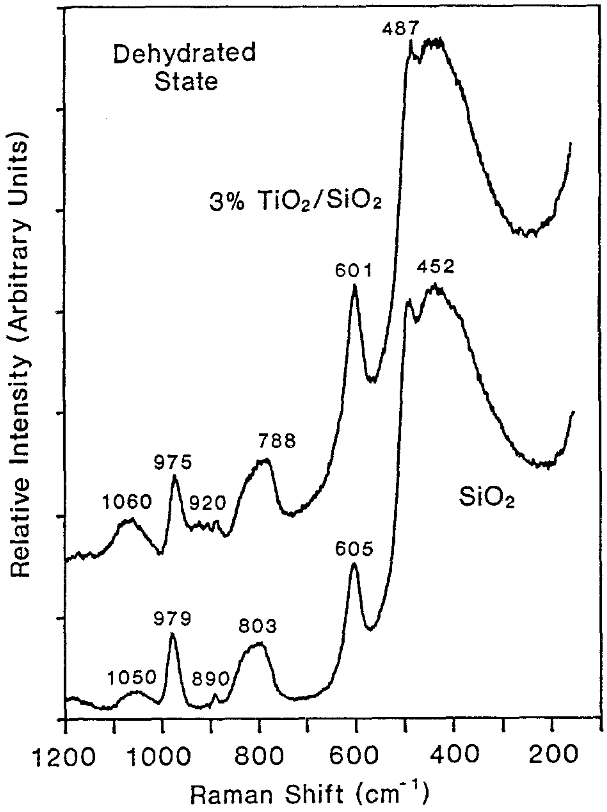

Fig. 1. The Raman spectra of the 3% TiO_2/SiO_2 catalyst and the SiO_2 support under *in situ* conditions.

RAMAN SPECTRA OF THE $V_2O_5/TiO_2/SiO_2$ CATALYSTS

In situ Raman spectra of the 0–3% vanadium oxide supported on 3% TiO_2/SiO_2 are shown in fig. 2. No crystalline V_2O_5 (major Raman bands at ~ 994, ~ 702, ~ 527, ~ 404, ~ 284, and ~ 146 cm^{-1}) or TiO_2 (anatase) (major Raman bands at ~ 144, ~ 399, ~ 520, ~ 640 cm^{-1}) are observed [17,21]. At low V_2O_5 loading on 3% TiO_2/SiO_2, a sharp and strong Raman band appears at ~ 1029 cm^{-1} which is characteristic of the dehydrated surface vanadium oxide species [7]. This Raman band shifts to ~ 1033 cm^{-1} and increases in intensity with increasing V_2O_5 loading. In addition, the weak and broad Raman band at ~ 924 shifts to ~ 905 cm^{-1}, and increases its intensity with increasing V_2O_5 loading. This weak band may be related to a trace of polymeric surface vanadia species [10,14].

The Raman spectrum of the 4% V_2O_5/40% TiO_2/SiO_2 catalyst under *in situ* conditions is presented in fig. 3 and exhibits a strong signal from bulk TiO_2 (anatase) (Raman bands at ~ 639, ~ 517, ~ 396, and ~ 149 cm^{-1}) in the 700–100 cm^{-1} region. In the high wavenumber region (1200–700 cm^{-1}), Raman bands at ~ 1032 and ~ 922 cm^{-1} are present. The dehydrated Raman features

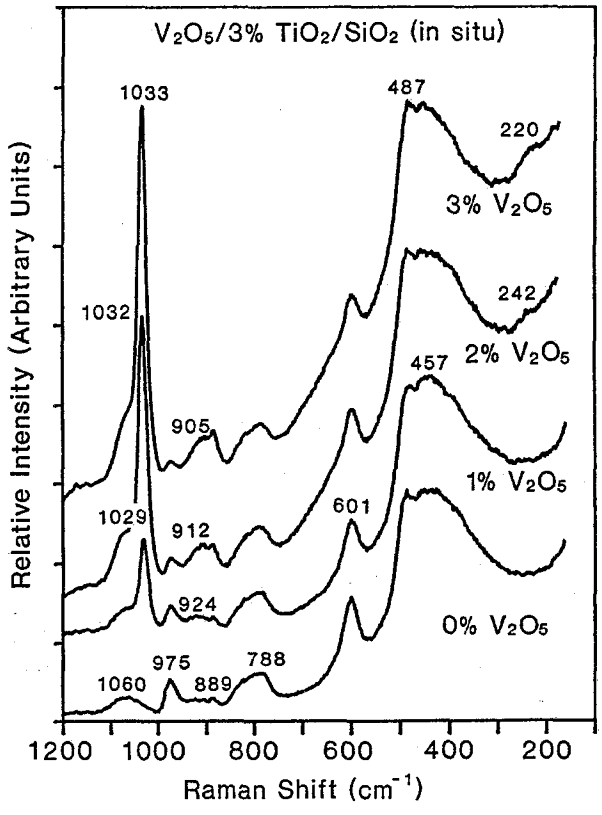

Fig. 2. The Raman spectra of the 0–3% V_2O_5/3% TiO_2/SiO_2 catalysts under *in situ* conditions.

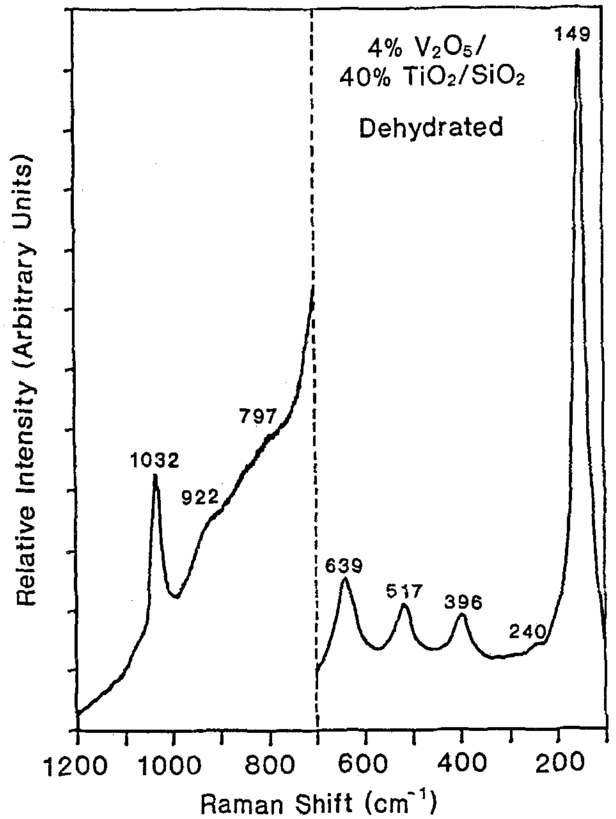

Fig. 3. The Raman spectra of the 4% $V_2O_5/40\%\ TiO_2/SiO_2$ catalyst under *in situ* conditions.

of the 4% $V_2O_5/40\%\ TiO_2/SiO_2$ catalyst are similar to the dehydrated surface vanadium oxide species present on bulk TiO_2 supports [6,9,11,14].

CATALYTIC STUDIES

The catalytic properties of the 1% V_2O_5/TiO_2, 1% V_2O_5/SiO_2, 3% TiO_2/SiO_2, and $V_2O_5/TiO_2/SiO_2$ catalysts during methanol oxidation are listed in table 1. Turnover number (TON) is defined as the number of CH_3OH molecules converted per V (or Ti) atom per sec. The catalytic studies reveal that the TON of the supported vanadium oxide on bulk TiO_2 (98% HCHO selectivity) is three orders of magnitude higher than the TON of the supported vanadium oxide on SiO_2 (79.2% HCHO and 17.9% CO/CO_2 selectivity) [7]. The surface titanium oxide overlayer on SiO_2 enhances the reactivity during methanol oxidation relative to the SiO_2 support which is essentially inactive and 100% selective to CO/CO_2 during methanol oxidation [7]. The deposition of 1–3% vanadium oxide on the 3% TiO_2/SiO_2 support increases the methanol oxidation activity of these catalysts by an order of magnitude relative to that of the support itself.

Table 1
The catalysis of methanol oxidation reaction over $V_2O_5/TiO_2/SiO_2$ catalysts

Catalyst	TON (sec^{-1})	FM	MF	Selectivity		
				DMM	DME	CO/CO_2
1% V_2O_5/TiO_2	1.8×10^{0}	98	–	1	1	–
1% V_2O_5/SiO_2	2.0×10^{-3}	79.2	–	–	2.9	17.9
3% TiO_2/SiO_2	1.5×10^{-2} *	39.8	49.0	1.6	1.7	7.9
1% V_2O_5/ 3% TiO_2/SiO_2	1.1×10^{-1}	83.4	8.7	3.7	2.0	2.2
2% V_2O_5/ 3% TiO_2/SiO_2	1.5×10^{-1}	92.5	1.8	2.7	1.7	1.3
3% V_2O_5/ 3% TiO_2/SiO_2	2.0×10^{-1}	91.1	2.3	2.2	1.2	3.2
4% V_2O_5/ 40% TiO_2/SiO_2	1.3×10^{0}	91.7	–	2.1	0.5	5.7

FM: HCHO; MF: $HCOOCH_3$; DMM: $(CH_3O)_2CH_2$; DME: CH_3OCH_3.
TON: number of CH_3OH molecule converted per V atom per sec.
TON *: number of CH_3OH molecule converted per Ti atom per sec.

In addition, the HCHO selectivity increases from ~ 40% to ~ 90% upon the addition of vanadium oxide. The 4% V_2O_5/40% TiO_2/SiO_2 catalyst, which contains bulk TiO_2 (anatase) particles, exhibits essentially the same TON as the V_2O_5/TiO_2 catalyst. However, the $V_2O_5/TiO_2/SiO_2$ catalyst possesses a selectivity of 92% HCHO and 5.7% CO/CO_2 compared to 98% HCHO and 0% CO/CO_2 for the V_2O_5/TiO_2 catalyst.

4. Discussion

Raman studies on the 0–3% V_2O_5/3% TiO_2/SiO_2 catalysts reveal that the deposition of vanadium and titanium oxides on the SiO_2 support results in a two-dimensional surface vanadium and titanium oxide overlayer due to the absence of crystalline V_2O_5 (major Raman bands at ~ 994, ~ 702, ~ 527, ~ 404, ~ 284, and ~ 146 cm^{-1}) and TiO_2 (anatase) (major Raman bands at ~ 640, ~ 520, ~ 399, ~ 144 cm^{-1}) [17,21]. The shifts of the supported titania Raman bands for the 3% TiO_2/SiO_2 catalyst and the supported vanadia Raman bands for the 1–3% V_2O_5/3% TiO_2/SiO_2 catalysts upon dehydration further confirm the formation of the surface titanium oxide and vanadium oxide species since previous *in situ* Raman studies have demonstrated that only two-dimensional surface metal oxide species are sensitive to moisture [6–10,22]. Bulk TiO_2 is found to be present on the 4% V_2O_5/40% TiO_2/SiO_2 catalyst. The presence of the surface vanadium oxide species on 40% TiO_2/SiO_2 is also confirmed by *in situ* Raman spectroscopy since the Raman bands are present at ~ 1032 and ~ 922 cm^{-1} upon dehydration.

Upon the deposition of vanadium oxide onto the 3% TiO_2/SiO_2 support, a new strong and sharp Raman band in the 1029–1033 cm^{-1} region as well as a new weak and broad Raman band in the 924–905 cm^{-1} are observed upon dehydration (see fig. 2). The Raman bands in the 1029–1033 cm^{-1} region are assigned to the dehydrated surface vanadium oxide species possessing a mono-oxo tetrahedral vanadate structure [6–10,14], and the Raman bands in the 924–905 cm^{-1} region are assigned to the dehydrated surface vanadium oxide species possessing a polymeric tetrahedral metavanadate structure [14]. For the 4% V_2O_5/40% TiO_2/SiO_2 catalyst containing bulk TiO_2 (anatase) particles, the Raman bands at ~ 1032 and ~ 920 cm^{-1} (see fig. 3) indicate that the same dehydrated surface vanadium oxide species as the V_2O_5/3% TiO_2/SiO_2 catalyst are also formed for this system. Thus, two dehydrated surface vanadium oxide species are present on the $V_2O_5/TiO_2/SiO_2$ catalysts.

The surface TiO_x species is present on the dehydrated V_2O_5/3% TiO_2/SiO_2 catalyst, and the surface TiO_x species as well as bulk TiO_2 (anatase) coexist on the dehydrated V_2O_5/40% TiO_2/SiO_2 catalyst. The similar Raman band at ~ 1030 cm^{-1} for the $V_2O_5/TiO_2/SiO_2$ systems and V_2O_5/TiO_2 [7] suggests that vanadium oxide interacts with the surface TiO_x species and bulk TiO_2 present on SiO_2 to form the surface vanadium oxide phase. The appearance of a second broad and weak Raman band in the 905–924 cm^{-1} region for the $V_2O_5/TiO_2/SiO_2$ systems also suggests that the surface VO_x species interact with surface TiO_x phase or bulk TiO_2 (anatase) particles since only one surface VO_x species (Raman band at ~ 1038 cm^{-1}) is present on SiO_2. The interactions between the surface vanadium oxide species and the surface TiO_x phase or bulk TiO_2 can be further discriminated by the catalytic studies as shown below.

The catalytic properties of the $V_2O_5/TiO_2/SiO_2$ catalysts were probed with the sensitive methanol oxidation reaction because of its ability to discriminate between surface acid sites (formation of dimethyl ether (CH_3OCH_3)), surface redox sites (formation of formaldehyde (HCHO) and methylformate ($HCOOCH_3$)), and surface basic sites (formation of CO/CO_2) [23]. The high selectivity towards HCHO and $HCOOCH_3$ over the $V_2O_5/TiO_2/SiO_2$ catalysts reveals that redox sites are predominant on the surface of these catalysts (with essentially no acid sites present). The TON of the surface vanadium oxide phase on a bulk TiO_2 support is three orders of magnitude higher than the TON of the surface vanadium oxide phase on SiO_2 which has been associated with the reducibility of the oxide supports [7]. The formation of a surface titanium oxide overlayer between the surface vanadia and the SiO_2 support increases the TON of methanol oxidation by two orders of magnitude relative to the V_2O_5/SiO_2 system due to the presence of the surface VO_x-TiO_2 interactions. Furthermore, the TON of the $V_2O_5/TiO_2/SiO_2$ catalyst containing bulk TiO_2 (anatase) particles is an order of magnitude higher than $V_2O_5/TiO_2/SiO_2$ catalysts not containing bulk TiO_2 (anatase) particles. The very similar TON of the 4% V_2O_5/40% TiO_2/SiO_2 sample and the 1% V_2O_5/TiO_2 indicates that the interactions between the surface VO_x species and crystalline TiO_2 are predominantly present on this catalyst which contains a significant amount of TiO_2 (anatase). Thus, the catalytic studies on the $V_2O_5/TiO_2/SiO_2$ catalysts suggest that the presence of the surface VO_x-TiO_2 interactions results in a more active catalyst than the surface VO_x-TiO_x interactions alone. The difference in reactivity between VO_x-TiO_2 and VO_x-TiO_x is probably due to the retardation of the reduction of the surface TiO_x species by their coordination to the silica support. Since the same *in situ* Raman band appears for the V_2O_5/TiO_2 and $V_2O_5/TiO_2/SiO_2$ catalysts, these results support the earlier conclusion that the different oxide supports only slightly perturb the vanadium-oxygen bond lengths of the surface vanadia species, however, the specific surface oxide-support interactions strongly affect the reactivity of the surface vanadia species [7]. This suggests that the surface V-O-Ti bridging bonds, rather than the surface V = O terminal bonds (Raman band at $\sim 1030\ cm^{-1}$), are associated with the active sites during oxidation reactions over supported vanadium oxide catalysts [7]. Furthermore, the current study demonstrates that apparently dispersed surface titania sites are also able to enhance the reactivity of surface vanadia species.

5. Conclusions

The molecular structure-reactivity relationships of the $V_2O_5/TiO_2/SiO_2$ catalysts were established in this investigation. Only the surface TiO_x species is present for the 3% TiO_2/SiO_2 catalyst, and the surface TiO_x species as well as bulk TiO_2 (anatase) coexist for the 40% TiO_2/SiO_2 catalyst. The deposition of 1–3% vanadium oxide onto 3% TiO_2/SiO_2 and 4% vanadium oxide onto 40% TiO_2/SiO_2 forms a surface vanadium oxide phase and no crystalline V_2O_5 is present. *In situ* Raman studies reveal that the surface vanadium oxide species, with an isolated vanadate structure possessing one terminal V = O bond (Raman bands at $\sim 1030\ cm^{-1}$) and three bridging V-O-support bonds, preferentially exists on the titania sites in the TiO_2/SiO_2 systems. The presence of a surface titanium oxide phase overlayer between the surface vanadium oxide and the SiO_2 support increases the methanol oxidation activity by two orders of magnitude relative to the V_2O_5/SiO_2 catalyst. The presence of bulk TiO_2 (anatase) particles in the $V_2O_5/TiO_2/SiO_2$ catalysts further increases the activity by an order magnitude relative to the $V_2O_5/TiO_2/SiO_2$ catalysts containing surface titanium oxide species, and its activity is similar to that of a 1% V_2O_5/TiO_2 catalyst. In addition, the $V_2O_5/TiO_2/SiO_2$ catalysts exhibit high selectivity towards HCHO because redox sites are predominant on the surface of these catalysts with essentially no acid sites present. The combined *in situ* Raman and catalytic studies reveal that the promotional effect of the oxide supports upon the surface vanadium oxide species is related to the specific surface V-O-support bonds.

Acknowledgments

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