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Raman characterization of alumina supported Mo–V–Fe catalysts: influence of calcination temperature

Jih-Mirn Jehng and Israel E. Wachs*

Zettlemoyer Center for Surface Studies, Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015 (USA); tel. (+1-215)7584274, fax. (+1-215)7583079

Fred. T. Clark and Mary. C. Springman

Amoco Oil Company, Amoco Research Center, P.O. Box 3011, Naperville, IL 60566 (USA)

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Abstract

Alumina supported V_2O_5, MoO_3, Fe_2O_3, Fe_2O_3-V_2O_5, and MoO_3-V_2O_5 catalysts were investigated by Raman spectroscopy as a function of calcination temperature under ambient conditions where the surfaces are hydrated. The single metal oxide systems (V_2O_5, MoO_3, or Fe_2O_3) and the mixed metal oxide systems (Fe_2O_3–V_2O_5 and MoO_3–V_2O_5) are present as surface metal oxide species on the alumina support at intermediate calcination temperatures. For the single metal oxide species, the surface vanadium oxide species consists of metavanadate species ($[VO_3]_n^{x-}$), the surface molybdenum oxide species consists of heptamolybdate ($Mo_7O_{24}^{6-}$) and octamolybdate ($Mo_8O_{26}^{4-}$) species, and the surface iron oxide species is primarily present as a surface spinel containing Fe^{3+} ions in the surface region of the alumina support. Addition of iron oxide and molybdenum oxide to the V_2O_5/Al_2O_3 transforms the surface metavanadate species to surface pyrovanadate species ($V_2O_7^{2-}$) and surface decavanadate species ($V_{10}O_{28}^{6-}$), respectively. The thermal stability of the supported metal oxide on the alumina support depends on the specific nature of the surface metal oxide species. The supported iron oxide on alumina has a high thermal stability, similar to the unpromoted alumina, which is probably related to Fe^{3+} absorption into the surface region of the alumina lattice. In contrast, the supported molybdenum oxide on alumina system is not stable above 800°C due to significant loss in the alumina surface area and volatilization of molybdenum oxide. The surface vanadium oxide species on alumina is stable up to a calcination temperature of 800°C and transforms to crystalline V_2O_5 at higher calcination temperatures due to significant loss in surface area of the alumina support. The mixed metal oxide species (Fe_2O_3-V_2O_5 and MoO_3-V_2O_5) on alumina could not stabilize the surface vanadium oxide on alumina above 800°, and accelerated the rate of surface area loss and phase transformations. No $FeVO_4$, $AlVO_4$, or V-Mo-O compounds were formed in these mixed metal oxide species on alumina at elevated temperatures.

Key words: alumina; calcination temperatures; iron oxide; molybdenum oxide; Raman spectroscopy; supported catalysts; vanadium oxide

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*Corresponding author.

Introduction

Supported V_2O_5 and MoO_3 catalysts have been found to be effective catalysts for many catalytic reactions such as selective oxidation and ammoxidation of hydrocarbons, selective reduction of NO_x, hydrodesulfurization and hydrocracking of crude oil, as well as isomerization and hydrogenation of alkenes [1–6]. The V_2O_5 and MoO_3 deposited on oxide supports (such as Al_2O_3, TiO_2, and SiO_2) form a two-dimensional surface vanadium oxide or molybdenum oxide overlayer [7–13]. The interaction of the surface vanadia (or molybdena) species and the oxide support has a pronounced effect on the catalytic properties of the supported vanadium oxide and molybdenum oxide catalysts. It is also known that these surface metal oxide species on oxide supports are stable to high calcination temperatures [13–16], and can prevent or accelerate the dehydroxylation as well as loss in surface area of the oxide supports [15–18].

Recent Raman studies on the supported vanadia catalysts with different vanadium oxide coverages reveal that the molecular structures of the surface vanadia species are influenced by the addition of a second metal oxide such as molybdenum oxide or iron oxide [19]. Under hydrated conditions, the transformation of surface metavanadate species (major Raman band at *ca.* 937 cm^{-1}) into surface pyrovanadate species (major Raman band at *ca.* 885 cm^{-1}) occurs upon the addition of the basic surface iron oxide species and the transformation of surface metavanadate species into surface decavanadate species (major Raman band at *ca.* 990 cm^{-1}) occurs upon the addition of the acidic surface molybdenum oxide species.

In the present study, Raman spectroscopy was used as the characterization technique to discriminate among the various metal oxide molecular structures of Mo, V, and Fe as well as provide information about the alumina support phases. A single surface metal oxide (5 wt.% Fe_2O_3, 5 wt.% V_2O_5, or 5 wt.% MoO_3) supported on Al_2O_3 and calcined from 500°C to 950°C was investigated by Raman spectroscopy in order to determine the thermal behavior of the surface metal oxide and alumina support phases during high calcination temperature treatments. The effect of a second metal oxide (5 wt.% MoO_3 or 5 wt.% Fe_2O_3) on the molecular structures and thermal behavior of the surface vanadium oxide (5 wt.% V_2O_5/Al_2O_3) and alumina support phases was also investigated by Raman spectroscopy as a function of calcination temperature.

Experimental

Materials

The precursors used in the preparation of the supported metal oxide catalysts were: ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 99.9 wt.% (Alfa, Danvers, MA); vanadium triisopropoxide, $VO(OC_3H_7)_3$ 95–99 wt.%

(Johnson Matthey, Ward Hill, MA); iron nitrate nano-hydrate (EM Science). The oxide supports used in this study were γ-Al_2O_3 (Harshaw, *ca.* 180 m^2/g) and PHF γ-Al_2O_3 (Cyanamid, *ca.* 196 m^2/g).

Preparations

The catalysts were prepared by the incipient-wetness impregnation method. For the non-air sensitive molybdenum precursor, an ammonium heptamolybdate/water solution was impregnated into the γ-Al_2O_3 (Harshaw) support. The wet samples were then dried at room temperature for 16 h, dried at 120°C for 16 h, and calcined at 500°C for 16 h. For the air sensitive vanadium precursor, a vanadium triisopropoxide (Alfa, 95–99 wt.%) in isopropanol (Mallinckrodt, 0.028 wt.% H_2O) solution was impregnated into the PHF γ-Al_2O_3 (Cyanamid) support under a nitrogen environment to avoid the crystallization of the precursor with atmospheric water, and the impregnated samples were kept in a glove box for 2 h to evaporate the excess alcohol. The samples were subsequently dried at 120°C for 16 h under flowing N_2 and calcined at 500°C under flowing dry air for 2 h.

The mixed MoO_3 and V_2O_5 on the γ-Al_2O_3 (Harshaw) support catalyst was prepared by a two stage impregnation method using the non-air sensitive molybdenum precursor for the first stage as mentioned above, and a vanadium triisopropoxide/methanol (Fisher Scientific, 99.9 wt.%) solution was then impregnated into the MoO_3/Al_2O_3 catalyst. The sample was subsequently dried at 120°C for 16 h under flowing N_2 and calcined at 500°C under N_2 gas for the first hour, then switched to the dry air for additional 15 h. Iron-based catalysts were prepared by dissolving iron nitrate nano-hydrate in methanol (Aldrich, 0.04 wt.% H_2O), drying overnight in flowing nitrogen using a small fixed-bed quartz tube, and calcining at 500°C for 2 h under flowing dry air. The mixed Fe_2O_3 and V_2O_5 on the PHF γ-Al_2O_3 (Cyanamid) support catalyst was prepared by first impregnating with vanadium precursor. After the drying procedures, the sample was impregnated with iron precursor, dried overnight in flowing nitrogen, and calcined at 500°C for 2 h under flowing dry air. All samples were further calcined at high temperatures from 700°C to 950°C for 2 h under flowing dry air.

Raman spectroscopy

Raman spectra were obtained with a Spex triplemate spectrometer (Model 1877) coupled to an EG&G intensified photodiode array detector which was cooled thermoelectrically to -35°C, and interfaced with an EG&G OMA III Optical Multichannel Analyzer (Model 1463). The samples were excited by the 514.5 nm line of an Ar^+ laser (Spectra Physics Model 171) with 10–100 mW power. The laser beam was focused on the sample disk, where the sample typically spins at about 2000 rpm to avoid local heating, 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 scattered Raman light was analyzed with an OMA III software package. The overall spectral resolution was determined to be better than 2 cm^{-1}. The detailed schematic diagram of the Raman spectrometer is described elsewhere [20].

Results and discussion

The molecular structures of the hydrated surface metal oxides were found to depend on the point of zero charge (PZC) or the net pH at which the surface possesses zero charge [9]. The PZC of a supported metal oxide system is determined by the combined pH of the oxide support and the metal oxide overlayer.

Consequently, oxide supports possessing a low pH at PZC, corresponding to an acidic environment, predominantly form octahedrally-coordinated surface vanadia species ($V_{10}O_{28}^{6-}$), and oxide supports possessing a high pH at pzc, corresponding to a basic environment, predominantly form tetrahedrally-coordinated surface vanadia species (VO_4^{3-}, $V_2O_7^{4-}$, and $(VO_3)_n^{x-}$) for supported vanadia catalysts [9]. The model of the net surface pH at PZC can also predict the molecular structures of other surface metal oxides (surface rhenium oxide, chromium oxide, molybdenum oxide, tungsten oxide, and surface niobium oxide) on various oxide supports under ambient conditions where these surfaces are hydrated [9,21].

Single metal oxide species on alumina

V_2O_5/Al_2O_3

The effect of calcination temperature on the Raman spectra of the 5 wt.% V_2O_5/Al_2O_3 (PHF) sample is shown in Fig. 1. The Raman bands at *ca.* 937, *ca.* 825, *ca.* 550, *ca.* 350, and *ca.* 220 cm^{-1} are characteristic of a hydrated surface vanadium oxide species which possesses a tetraherally-coordinated metavan-

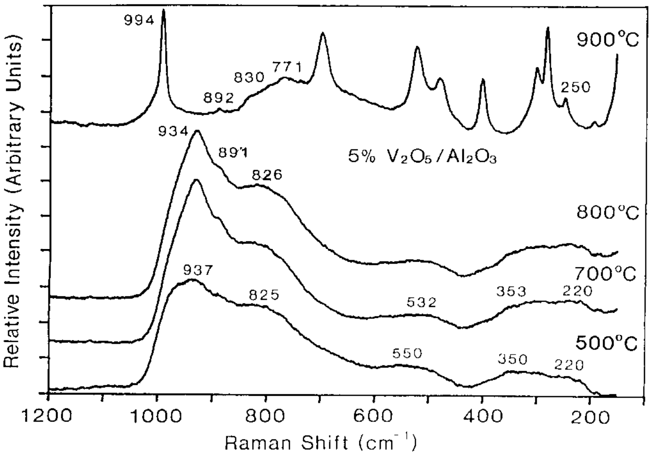

Fig. 1. The Raman spectra of 5 wt.% V_2O_5/Al_2O_3 as a function of calcination temperature.

adate structure [8,9]. The surface vanadium oxide species is stable to a temperature of 800 °C, however, after the 900 °C calcination treatment the surface vanadium oxide species transforms to crystalline V_2O_5 (Raman bands at *ca.* 994, *ca.* 702, *ca.* 527, *ca.* 404, and *ca.* 284 cm^{-1}). In addition, the transformation of γ-alumina to δ or θ-alumina is also detected by the appearance of a Raman band at *ca.* 250 cm^{-1} which is characteristic of δ and θ alumina phases [8,22,23]. XRD analysis confirms that a θ-alumina phase as well as a trace of crystalline V_2O_5 are present after the 900 °C treatment [24]. The BET surface area of the 5 wt.% V_2O_5/Al_2O_3 (PHF) sample decreased from 191 to 44 m^2/g as the calcination temperature increased from 500 to 900 °C (see Table 1). This suggests that the presence of the surface vanadium oxide species accelerates the surface area loss of the alumina support, since relatively little surface area loss occurred on the pure alumina (PHF) calcined at 900 °C (from *ca.* 191 to *ca.* 161 m^2/g, see Table 1). The broad Raman feature appearing at *ca.* 771 cm^{-1} is assigned to a monomeric tetrahedral species with a longer V–O bond due to the presence of sodium ions on the θ-alumina surface [8]. The presence of monomeric tetrahedral vanadia species also indicates that the phase transformation of γ-Al_2O_3 to θ-Al_2O_3 was accompanied by some surface segregation of sodium [8]. Sodium is usually present as a trace impurity in alumina, and the surface sodium concentration increases from γ to α-Al_2O_3 due to the migration of sodium from the bulk to the surface of alumina at high calcination temperature [8]. Solid state ^{51}V-NMR studies on the 5 wt.% V_2O_5/Al_2O_3 (PHF) sample at different temperature treatments in 500–900 °C are also in agreement with the above Raman results [24]. Thus, the surface vanadium oxide species are stable up to 800 °C calcination treatments, and the transformations of the surface vanadia species to crystalline V_2O_5 as well as γ-Al_2O_3 to θ-Al_2O_3 occur between 800 °C and 900 °C.

TABLE 1

Effects of the surface metal oxides and calcination temperature on the alumina support surface area

Catalyst	BET surface area (m^2/g) at various temperatures (°C)		
	500	900	950
alumina (Harshaw)	180	-	94
alumina (PHF)	191	161	-
5 wt.% V_2O_5/Al_2O_3 (PHF)	191	44	-
5 wt.% MoO_3/Al_2O_3 (Harshaw)	180	-	34
5 wt.% Fe_2O_3/Al_2O_3 (PHF)	184	157	-
5 wt.% Fe_2O_3/5 wt.% V_2O_5/Al_2O_3 (PHF)	190	6	-
5 wt.% MoO_3/5 wt.% V_2O_5/Al_2O_3 (Harshaw)	180	1.1	-

MoO_3/Al_2O_3

The influence of calcination temperature on the Raman spectra of the 5 wt.% MoO_3/Al_2O_3 (Harshaw) sample is presented in Fig. 2. The Raman bands at *ca.* 950, *ca.* 850, *ca.* 320, and *ca.* 215 cm^{-1} are characteristic of a hydrated surface molybdenum oxide species which possesses an octahedrally-coordinated structure (a mixture of $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ [6,9,11,12,25]. Raman studies reveal that only surface molybdenum oxide species are present up to 950°C, and no crystalline MoO_3 (major Raman bands at *ca.* 994 and *ca.* 820 cm^{-1}) or the compound $Al_2(MoO_4)_3$ (major Raman bands at *ca.* 1037, *ca.* 1004, and *ca.* 380 cm^{-1}) are present. Recent high resolution NMR studies on the 18 wt.% MoO_3/Al_2O_3 sample calcined at about 700°C suggest that the compound $Al_2(MoO_4)_3$ forms on the alumina surface at high molybdenum oxide loadings [26]. Thus, the absence of the compound $Al_2(MoO_4)_3$ for the 5 wt.% MoO_3/Al_2O_3 sample at 950°C is probably due to the low molybdenum oxide coverage or the decomposition of the compound $Al_2(MoO_4)_3$ at this high calcination temperature. Upon calcination at 800°C, a trace of δ or θ-alumina is also detected by the appearance of a weak Raman band at *ca.* 250 cm^{-1}. After the 950°C calcination treatment, all the Raman bands in the 850–200 cm^{-1} region are characteristic of the δ or θ-alumina phase. In addition, the BET surface area measurements on the 5 wt.% MoO_3/Al_2O_3 (Harshaw) sample calcined at 950°C reveal that the presence of the surface molybdenum oxide species accelerate the surface area loss of the alumina support (from *ca.* 180 to *ca.* 34 m^2/g, see Table 1) compared to the surface area loss of the pure alumina (Harshaw) calcined at 950°C (from *ca.* 180 to *ca.* 94 m^2/g, see Table 1). However, only 1 wt.% MoO_3 remains on the alumina support after the 950°C calcination treatment, and the surface density of surface molybdates in the 5 wt.% MoO_3/Al_2O_3 sample calcined at 950°C (*ca.* 1.23×10^{20} Mo atom/m^2) remains ap-

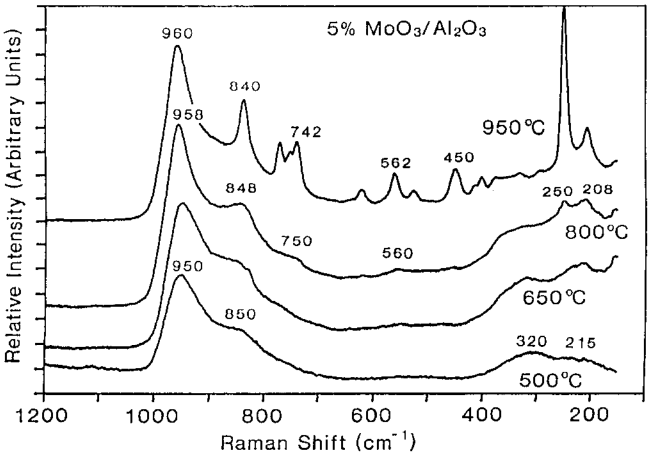

Fig. 2. The Raman spectra of 5 wt.% MoO_3/Al_2O_3 as a function of calcination temperature.

proximately the same as that calcined at 500°C (*ca.* 1.16×10^{20} Mo atom/m^2). The Mo content of the catalyst was determined by ICP analysis [18].

Consequently, the volatilization of crystalline MoO_3 at high temperatures results in the absence of crystalline MoO_3 for the MoO_3/Al_2O_3 (Harshaw) sample calcined at 950°C.

Fe_2O_3/Al_2O_3

The Raman spectra of the 5 wt.% Fe_2O_3/Al_2O_3 (PHF) sample as a function of calcination temperature are shown in Fig. 3. The weak Raman bands at *ca.* 610, *ca.* 500, *ca.* 410, *ca.* 297, and *ca.* 220 cm^{-1} are characteristic of a trace of crystalline α-Fe_2O_3 (see the reference Raman spectra for iron oxide compounds in Table 2), and the Raman intensities of these bands are not affected by high temperature calcination treatments. An additional broad Raman band at *ca.* 750 cm^{-1} for the 5 wt.% Fe_2O_3/Al_2O_3 sample calcined at 500°C does not

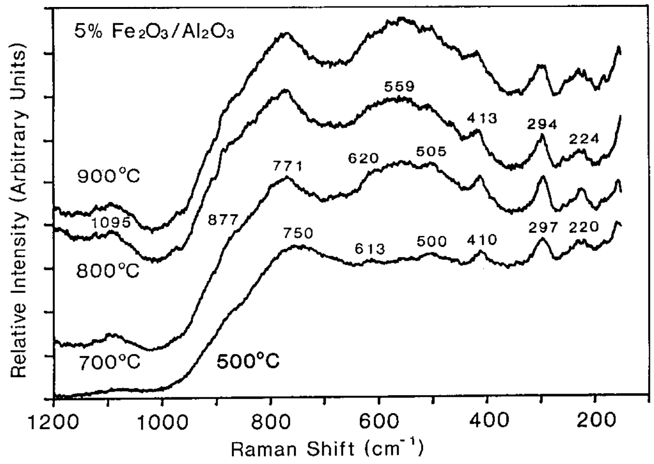

Fig. 3. The Raman spectra of 5 wt.% Fe_2O_3/Al_2O_3 as a function of calcination temperature.

TABLE 2

Raman bands of iron oxide compounds

Compound	Raman bands (cm^{-1})
Fe_3O_4	662(s), 532(w)
γ-Fe_2O_3	676(s), 468(w), 390(w), 124(s)
α-Fe_2O_3	605(m), 493(w), 403(m), 289(s), 221(s) 127(m)
$FeAl_{2.1}O_4$	676(m), 622(m), 512(w), 418(m), 299(s) 232(m)
$FeVO_4$	960(m), 930(s), 890(s), 840(s), 760(w) 730(s), 650(w), 450(w), 370(w), 320(w)

match any reference iron oxide compounds in Table 2 and is assigned to a surface iron oxide species. Complementary Mössbauer studies suggest that Fe^{3+} ions are present on the alumina surface [24].

Increasing the calcination temperature somewhat enhances the intensities of the Raman bands at *ca.* 770 and *ca.* 560 cm^{-1} and is probably related to the distortion of the surface iron oxide species. It appears that the surface iron oxide species are stable to high calcination temperatures, and no indications of the phase transformation from γ-alumina (Raman inactive) to δ,θ-alumina (Raman bands at *ca.* 837 (m), *ca.* 753 (m) , and *ca.* 251 (s) cm^{-1}) is observed [8]. The stability of the alumina support for the 5 wt.% Fe_2O_3/Al_2O_3 sample under high temperature treatments was also confirmed by XRD and BET measurements [24]. The molecular structure of the surface iron oxide species is not expected to be a function of the surface pH of PZC because it is not present as a hydrated overlayer, but is incorporated into the surface of the alumina support. Thus, the absorbed Fe^{3+} ions and a trace of crystalline α-Fe_2O_3 coexist on the alumina support at all temperatures.

In summary, the above studies demonstrate that the metal oxides are atomically dispersed on the alumina support after preparation at 500°C, with the exception of a trace of Fe_2O_3 crystallites, and that the thermal stability of the supported metal oxide catalyst depends on the specific nature of the surface metal oxide species. In Table 1, the Fe_2O_3/Al_2O_3 (PHF) sample retains 85% of its surface area and does not undergo an alumina phase transition after calcination at 900°C. However, the V_2O_5/Al_2O_3 (PHF) system calcined at 900°C possesses only 23% of the surface area of the original alumina (PHF) support and the surface vanadia species are transformed to crystalline V_2O_5. Similarly, the MoO_3/Al_2O_3 (Harshaw) system calcined at 950°C possesses only 19% of the surface area of the original alumina (Harshaw) support and the surface molybdena species are transformed to crystalline MoO_3 which are volatile. The surface metal oxide species which remain coordinated to the support are stable to high calcination temperatures due to a strong interaction with the oxide support. The phase transformation of γ-alumina to δ or θ-alumina also accompanies the loss in surface area for the alumina supported vanadia and molybdena catalysts at high temperature treatments.

Mixed metal oxide species on alumina

$Fe_2O_3/V_2O_5/Al_2O_3$

The 5 wt.% Fe_2O_3/5 wt.% V_2O_5/Al_2O_3 (PHF) sample calcined at 500°C transforms a majority of the hydrated surface metavanadate species (major Raman band at *ca.* 937 cm^{-1}) into the hydrated surface pyrovanadate species (major Raman band at *ca.* 885 cm^{-1}) due to the basic nature of the surface iron oxide [19]. At higher calcination temperatures (700–800°C), the surface metavanadate (major Raman band at *ca.* 932 cm^{-1}) and surface pyrovanadate (major Raman band at *ca.* 892 cm^{-1}) species coexist on the alumina support under ambient conditions as shown in Fig. 4. A monomeric tetrahedral vana-

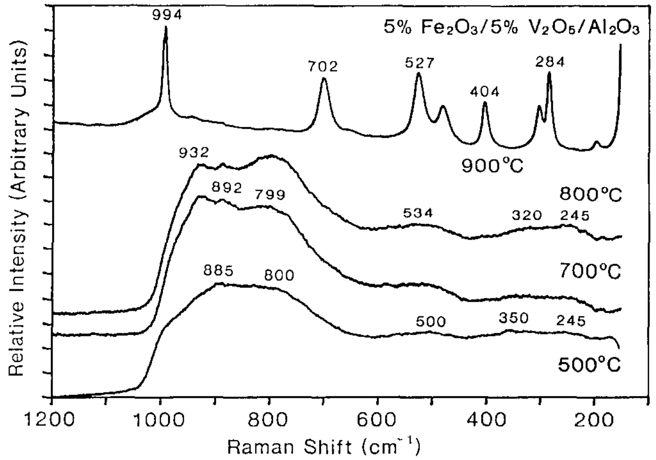

Fig. 4. The Raman spectra of 5 wt.% Fe_2O_3/5 wt.% V_2O_5/Al_2O_3 as a function of calcination temperature.

dium oxide species with a Raman band at *ca.* 800 cm^{-1} is also present on the surface, and its intensity increases with increasing calcination temperature. After the 900°C calcination treatment, crystalline V_2O_5 is formed on the alumina surface. No information about the alumina support is provided because the color of the sample prevents detection of the phase of the underlying alumina support. XRD studies on this $Fe_2O_3/V_2O_5/Al_2O_3$ mixed oxide catalyst indicate that the γ-Al_2O_3 phase is transformed into the δ,κ-Al_2O_3 phase after this thermal treatment. Raman, XRD, and ^{51}V-NMR studies are in agreement with the presence of crystalline V_2O_5 for the mixed $Fe_2O_3/V_2O_5/Al_2O_3$ system after the 900°C calcination treatment [24]. In addition, the BET surface area measurements on the 5 wt.% Fe_2O_3/5 wt.% V_2O_5/Al_2O_3 sample calcined at 900°C reveal that the presence of iron oxide further accelerates the surface area loss of the mixed $Fe_2O_3/V_2O_5/Al_2O_3$ system (from *ca.* 190 to *ca.* 6 m^2/g, see Table 1) compared to the surface area loss of the 5 wt.% V_2O_5/Al_2O_3 sample calcined at 900°C (from *ca.* 191 to *ca.* 44 m^2/g, see Table 1). The strong Raman cross-section of vanadium oxide overshadows the Raman signal of iron oxide.

Raman studies reveal that multiple surface vanadium oxide species are present on the alumina surface under ambient conditions, and their relative concentrations are dependent on the calcination temperature. The presence of Fe^{3+} ions in the V_2O_5/Al_2O_3 system as a solid solution was determined by Mössbauer spectroscopy [24]. The addition of the basic iron oxide into the hydrated V_2O_5/Al_2O_3 system also affects the molecular structures of the surface vanadium oxide species, and preferentially forms the surface pyrovanadate species (major Raman band at *ca.* 892 cm^{-1}) or the surface monomeric tetrahedral vanadium oxide species (major Raman band at *ca.* 800 cm^{-1}). The surface vanadium oxide species are stable up to a temperature of 800°C. No

$FeVO_4$ or $AlVO_4$ compounds are detected on the alumina surface by Raman, XRD, and ^{51}V-NMR measurements.

$MoO_3/V_2O_5/Al_2O_3$

Comparison of the hydrated Raman spectra of V_2O_5/Al_2O_3 (Fig. 1) and $MoO_3/V_2O_5/Al_2O_3$ (Fig. 5) reveals that the addition of the molybdenum oxide to the V_2O_5/Al_2O_3 system converts the surface metavanadate species (major Raman band at *ca.* 937 cm^{-1}, see Fig. 1) into the surface decavanadate species (a shoulder on the Raman band at *ca.* 990 cm^{-1}, see Fig. 5) due to the acidic nature of the surface molybdenum oxide species. The hydrated surface decavanadate species, with a $V_{10}O_{28}^{6-}$ structure, and the hydrated surface molybdenum oxide species, with a $Mo_8O_{26}^{4-}$ structure, coexist on the alumina support [19]. Upon increasing the calcination temperature to 700°C, the surface decavanadate species (a shoulder on the Raman band at *ca.* 990 cm^{-1}) and the surface molybdenum oxide species (major Raman band at *ca.* 960 cm^{-1}) are stable on the alumina surface as shown in Fig. 5. At the higher calcination temperature of 800°C, the disappearance of the Raman band at *ca.* 960 cm^{-1} and the absence of the Raman features of crystalline MoO_3 indicate that volatilization of the surface molybdenum oxide species has occurred. After the 900°C calcination treatment, a small amount of crystalline V_2O_5 (Raman bands at *ca.* 991, *ca.* 700, *ca.* 520, *ca.* 405, *ca.* 282, and *ca.* 148 cm^{-1}) is present and a monomeric tetrahedral vanadate species (Raman band at *ca.* 760 cm^{-1}) is also present due to the loss in surface area and surface segregation of sodium ions at these high temperatures [8], respectively. In addition, the $MoO_3/V_2O_5/Al_2O_3$ (Harshaw) system calcined at 900°C possesses only 0.6% of the surface area of the original alumina (Harshaw) support (see Table 1) [18].

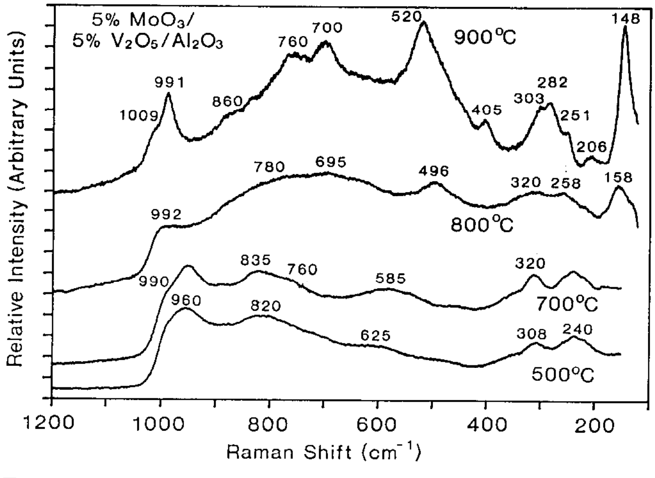

Fig. 5. The Raman spectra of 5 wt.% MoO_3/5 wt.% V_2O_5/Al_2O_3 as a function of calcination temperature.

Raman studies on the $MoO_3/V_2O_5/Al_2O_3$ system reveal that the hydrated surface vanadium oxide as well as the hydrated molybdenum oxide species coexist on the alumina surface. The presence of an acidic molybdenum oxide in the V_2O_5/Al_2O_3 system affects the molecular structures of the surface vanadium oxide species, and preferentially forms the surface decavanadate species (major Raman band at *ca.* 990 cm^{-1}). The surface vanadium oxide species are stable up to a temperature of 800°C but the surface molybdenum oxide species become volatile at this temperature.

The above studies demonstrate that the mixed metal oxides are atomically dispersed on the alumina support after preparation at 500°C, and that no bulk mixed oxide phases ($FeVO_4$ or V–Mo–O compounds) are present. Addition of iron oxide and molybdenum oxide affected the surface vanadium oxide molecular structure and thermal stability of the supported mixed metal oxide system. The various vanadium oxide molecular structures present under ambient conditions in the supported vanadium oxide catalysts are summarized in Table 3 as a function of catalyst composition and calcination temperature. The addition of iron oxide to the supported vanadium oxide catalyst favored the transformation of surface metavanadate species to surface decavanadate species. These structural transformations are due to the changes in the net pH at surface point of zero charge of these hydrated overlayers [9]. In all cases, calcination at 500–950°C resulted in the transformation of the majority of the surface vanadium oxide species to crystalline V_2O_5 due to the significant loss in surface area of the catalysts at these temperatures. Comparison of the BET surface areas of the above mixed metal oxide species on the alumina support calcined at 900°C indicates that the mixed $Fe_2O_3/V_2O_5/Al_2O_3$ system has greater thermal stability than the $MoO_3/V_2O_5/Al_2O_3$ system (see Table 1).

TABLE 3

Influence of second metal oxide and calcination temperature (calc. temp.) on hydrated surface vanadate phases on alumina

Catalyst	Calc. temp. (°C)	Monomer, ortho-VO_4	Dimer, pyro- ($V_2O_7^{4-}$)	Polymer, meta- $(VO_3)_n$	Cluster, deca- ($V_{10}O_{28}^{6-}$)	Bulk V_2O_5
5% V_2O_5/Al_2O_3	500-800	-	-	major	-	-
	900	trace	[a]	[a]	[a]	major
5% V_2O_5/5% Fe_2O_3/Al_2O_3	500	minor	major	minor	-	-
	700-800	moderate	moderate	moderate	-	-
	900	[a]	[a]	[a]	[a]	major
5% V_2O_5/5% MoO_3/Al_2O_3	500-800	-	-	-	major	-
	900	minor	-	-	-	major

[a] A surface vanadate exists, however spectra are dominated by crystalline V_2O_5.

The accelerated surface area loss of the mixed metal oxide systems compared to the single metal oxide systems is probably due to the enhanced surface diffusion of vanadia species and sintering of the alumina support at higher calcination temperatures [24]. Consequently, the thermal stability of a supported metal oxide system is dependent on the surface metal oxide–support interaction.

Conclusions

The formation of a single surface metal oxide species (V_2O_5, Fe_2O_3, or MoO_3) and mixed surface metal oxide species (Fe_2O_3–V_2O_5 or MoO_3–V_2O_5) on the alumina support at intermediate temperatures (500–800 °C) were determined by Raman spectroscopy under ambient conditions where the surfaces are hydrated. The single metal oxide species (V_2O_5, MoO_3, or Fe_2O_3) and the mixed metal oxide species (Fe_2O_3–V_2O_5 and MoO_3–V_2O_5) are present as surface metal oxide species on the alumina support at intermediate calcination temperatures. For the single metal oxide species, the surface vanadium oxide species consists of metavanadate species ($[VO_3]_n^{x-}$), the surface molybdenum oxide species consists of heptamolybdate ($Mo_7O_{24}^{6-}$) and octamolybdate ($Mo_8O_{26}^{4-}$) species, and the surface iron oxide species is primarily present as a surface spinel containing Fe^{3+} ions in the surface region of the alumina support. Addition of iron oxide and molybdenum oxide to the V_2O_5/Al_2O_3 transforms the surface metavanadate species to surface pyrovanadate species ($V_2O_7^{2-}$) and surface decavanadate species ($V_{10}O_{28}^{6-}$), respectively. The thermal stability of the supported metal oxide on the alumina support depends on the specific nature of the surface metal oxide species. The supported iron oxide on alumina has the highest thermal stability among these catalysts, similar to that of the unpromoted alumina support. In contrast, the system of molybdenum oxide supported on alumina is not stable above 800 °C due to a significant loss in the alumina surface area and volatilization of molybdenum oxide. The surface vanadium oxide species on alumina is stable up to a calcination temperature of 800 °C and transforms to crystalline V_2O_5 at higher calcination temperatures due to a significant loss in surface area of the alumina support. The mixed metal oxide species (Fe_2O_3–V_2O_5 and MoO_3–V_2O_5) on alumina could not stabilize the surface vanadium oxide on alumina above 800 °C, and accelerated the rate of surface area loss and phase transformations. No $FeVO_4$, $AlVO_4$, or V–Mo–O compounds were formed in these mixed metal oxide species on alumina at elevated temperatures.

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