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Raman spectroscopy of V_2O_5 , MoO_3 , Fe_2O_3 , $MoO_3-V_2O_5$, and $Fe_2O_3-V_2O_5$ supported on alumina catalysts: influence of coverage and dehydration

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Abstract

In the present investigation the influence of addition of molybdenum oxide and iron oxide to a 5% V_2O_5/Al_2O_3 sample has been studied by Raman spectroscopy under ambient as well as dehydrated conditions. The results show that under ambient conditions the presence of both vanadium oxide and molybdenum oxide on the hydrated alumina surface results in the conversion of hydrated metavanadate species into hydrated decavanadate species and of hydrated MoO_4^{2-} species into hydrated octahedrally coordinated clusters. This is due to the decrease in the net pH at point of zero charge relative to the individual metal oxide systems. For the mixed $Fe_2O_3-V_2O_5/Al_2O_3$ sample it has been found that under ambient conditions the hydrated metavanadate species are converted into hydrated pyrovanadate and orthovanadate species, which is ascribed to the basic nature of the surface iron oxide species. Under dehydrated conditions the presence of both vanadium oxide and molybdenum oxide on the alumina surface results in increased concentrations of surface vanadate and molybdate species, which are found at much higher surface coverage in the corresponding individual metal oxide systems. A similar effect has been observed in the presence of iron oxide, which also promotes the formation of a moderately distorted vanadium oxide species.

Introduction

Supported vanadium oxide catalysts are used extensively in industry for selective oxidations [1–3], ammoxidation of hydrocarbons [4–6] and selective reduction of NO_x [7]. It has been reported that addition of a second metal oxide such as molybdenum oxide or iron oxide to the supported vanadium oxide system enhances the activity and selectivity for the $NO_x + NH_3 + O_2$ reaction [7, 8]. On the other hand, molybdenum oxide supported on alumina catalysts is used as a hydrotreating catalyst to remove S and N from petroleum

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feeds [9]. These petroleum feeds are contaminated with traces of Fe and V that are deposited on the catalysts. The working catalyst is present as a sulfide, but needs to be regenerated to remove the carbon that accumulates and deactivates the catalyst. It is during the regeneration that Fe, V and Mo (usually Ni and Co are also present) get converted to their oxides and dramatically degrade the properties of the hydrotreating catalyst [10].

This knowledge has led to much interest in the molecular structures of these supported metal oxides. Raman studies, combined with FT-IR and solid-state ^{51}V NMR studies in the case of supported vanadium oxide and combined with UV-Vis spectroscopy in the case of supported molybdenum oxide, revealed that the surface structures of these supported metal oxides are a function of the surface coverage, support type, surface hydration, surface impurities and calcination temperature [11–45]. For the $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ systems, it was demonstrated that molybdenum oxide and vanadium oxide form two-dimensional surface overlayers up to surface coverages of 20% MoO_3 and 20% V_2O_5 , respectively [12, 31–34]. Under ambient conditions, water molecules are adsorbed on the surface, and consequently, the surface molybdenum and vanadium oxide species are hydrated; their molecular structures are similar to those found in aqueous solutions of molybdenum and vanadium oxide, respectively [12, 31–34]. Under *in situ* conditions, the adsorbed moisture desorbs upon heating and the surface becomes dehydrated. For the $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ systems, the surface structures of molybdenum oxide and vanadium oxide, respectively, are drastically altered upon dehydration [33–42, 44, 45], and this is a direct confirmation that both metal oxides form a two-dimensional surface overlayer on the alumina support. The supported iron oxide system has not been characterized by Raman spectroscopy, but was studied by Mössbauer spectroscopy [46–48]. For $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, spectral doublets with rather broad absorption lines of the iron(III) oxide species were detected and ascribed to bulk $\alpha\text{-Fe}_2\text{O}_3$ and Fe^{3+} in solid solution in the alumina support.

Although the surface structures of the single-component $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ systems have been well characterized by Raman spectroscopy and some structural information is available for the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ system from Mössbauer spectroscopy, the surface structures of mixed $\text{MoO}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ systems are not well understood. Chary *et al.* studied the $\text{MoO}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system by X-ray diffraction and oxygen chemisorption and found that addition of molybdenum oxide decreases the dispersion of the vanadium oxide phase [49]. No characterization studies have been reported for the mixed $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system to date.

The purpose of the present study is to determine the influence of addition of molybdenum oxide and iron oxide on the supported vanadium oxide structures. Therefore, we have studied the single-component $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ systems as well as the mixed $\text{MoO}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$ systems with Raman spectroscopy under ambient and *in situ* dehydrated conditions as a function of the metal oxide loadings.

Experimental

Preparation of the catalysts

The support used in this study was γ -alumina (Harshaw, $180 \text{ m}^2 \text{ g}^{-1}$). The $\text{MoO}_3/\text{Al}_2\text{O}_3$ samples and 5% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample were prepared by (incipient wetness) impregnation of an aqueous solution of ammonium heptamolybdate and ferric nitrate, respectively. After the impregnation step, the samples were dried at room temperature, at $120 \text{ }^\circ\text{C}$, and finally calcined in dry air at $500 \text{ }^\circ\text{C}$ overnight. The vanadium oxide samples were prepared by (incipient wetness) impregnation with a solution of vanadium triisopropoxide (Alpha, 95–98% purity) in methanol. Owing to the air and moisture sensitive nature of this alkoxide precursor, the impregnation, subsequent drying at room temperature and heating at $350 \text{ }^\circ\text{C}$ were performed under a nitrogen atmosphere. The samples were finally calcined in dry air at $500 \text{ }^\circ\text{C}$ overnight. The mixed $\text{MoO}_3\text{--V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5/\text{Al}_2\text{O}_3$ samples were prepared from the $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples, respectively, by adding the vanadium oxide as described above. The surface coverages are expressed in wt.% of the metal oxide.

Raman studies

The Raman apparatus consists of a triplemate spectrometer (Spex 1877) coupled to an optical multichannel analyzer (Princeton Applied Research 1463) equipped with an intensified photodiode array detector (1024 pixels, cooled to $-35 \text{ }^\circ\text{C}$). For Raman studies under ambient conditions, the samples were pressed onto KBr and spun at 2000 rpm. *In situ* Raman spectra were recorded from stationary samples pressed into self-supporting wafers. A modified version of an *in situ* cell, developed by Wang and Hall [43], was used in all the experiments under dehydrated conditions. The sample was heated to $500 \text{ }^\circ\text{C}$ in $\approx 30 \text{ min}$ and held for 30 min. Then the sample was cooled down to $\approx 50 \text{ }^\circ\text{C}$ in $\approx 45 \text{ min}$. At this temperature the Raman spectrum was recorded. Ultra-high-purity hydrocarbon-free oxygen (Linde Gas) was purged through the cell during the experiment. The acquisition time used per scan was 30 s, and 25 scans were averaged. The 514.5 nm line of an argon ion laser (Spectra Physics) was used as the excitation source. The laser power at the sample was 10–40 mW.

Results and discussion

Several studies have revealed that hydration drastically affects the structure of supported metal oxides [11–16, 18, 19, 25–30, 33–45]. Therefore, it is necessary to present and discuss the Raman spectra recorded under ambient conditions (where the metal oxides are hydrated) separately from those recorded under dehydrated conditions.

*Ambient conditions**V₂O₅/Al₂O₃ and MoO₃/Al₂O₃*

The Raman spectra of the single-component V₂O₅/Al₂O₃ and MoO₃/Al₂O₃ systems under ambient conditions have been fully reported in previous investigations [31, 32, 34]. For understanding the mixed MoO₃-V₂O₅/Al₂O₃ and Fe₂O₃/Al₂O₃ systems, it is sufficient to recall here that for the V₂O₅/Al₂O₃ system, hydrated metavanadate surface species (VO₃)_n, are present at low loadings, while hydrated decavanadate species, V₁₀O₂₈⁶⁻, are found at higher surface coverage [12, 18, 32, 33]. Furthermore, the MoO₃/Al₂O₃ samples show the presence of hydrated MoO₄²⁻ surface species at low surface coverage, while hydrated octahedrally coordinated clusters (Mo₇O₂₄⁶⁻ or Mo₈O₂₆⁴⁻ are observed at higher loading [12, 34]. These hydrated vanadium oxide and molybdenum oxide structures are also found in aqueous solutions of vanadium oxide and molybdenum oxide, respectively, where the molecular structures depend on the solution pH and concentration [50]. This similarity exists since under ambient conditions the surface of the oxide support is hydrated and the surface metal oxide overlayer is essentially in an aqueous medium. Recently, Deo and Wachs developed a model that predicts the molecular structures of supported metal oxides (such as vanadium, tungsten, molybdenum, rhenium and chromium) under ambient conditions [32]. It was found that the metal oxide surface structures are dependent on the net pH at which the surface possesses zero surface charge (pzc). The net surface pH at pzc is determined by the specific support (titania, alumina, silica, etc.) and the surface coverage of the metal oxide. The addition of surface vanadium oxide (pH ≈ 1.4) or molybdenum oxide (pH ≈ 1.5) to alumina (pH ≈ 8) always decreases the surface pH of the hydrated surface, and the decrease is proportional to the surface vanadium oxide or molybdenum oxide coverage, respectively.

MoO₃-V₂O₅/Al₂O₃

Three mixed MoO₃-V₂O₅/Al₂O₃ samples were prepared in order to examine the interaction between vanadium oxide and molybdenum oxide species on the alumina surface, and their Raman spectra are presented in Fig. 1. The vanadium oxide loading is maintained at 5% and the molybdenum oxide loading increases from 0 to 10%. In the absence of molybdenum oxide, the Raman spectrum shows bands at 940, ≈ 825, ≈ 550, ≈ 350 and ≈ 220 cm⁻¹, which have been assigned to hydrated metavanadate species [12, 18, 31, 32]. The Raman spectrum of the 1% MoO₃-5% V₂O₅/Al₂O₃ sample shows that the stretching mode is shifted upward to 945 cm⁻¹ and that in the low-wavenumber region new bands at 315, 240 and 180 cm⁻¹ are present. The upward shift and especially the bands in the low-wavenumber region are indicative of the presence of hydrated decavanadate species [31, 32]. Since the stretching mode is observed at 945 cm⁻¹, it is likely that some metavanadate species are also present in this sample. The 5% MoO₃-5% V₂O₅/Al₂O₃ and 10% MoO₃-5% V₂O₅/Al₂O₃ samples show bands at ≈ 985 (shoulder), 960, 820, ≈ 360, 315, ≈ 230 and 180 cm⁻¹. These bands indicate the presence

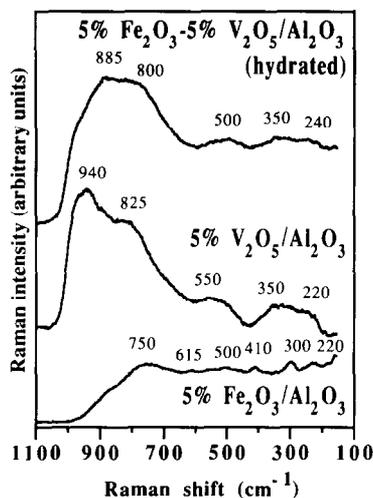
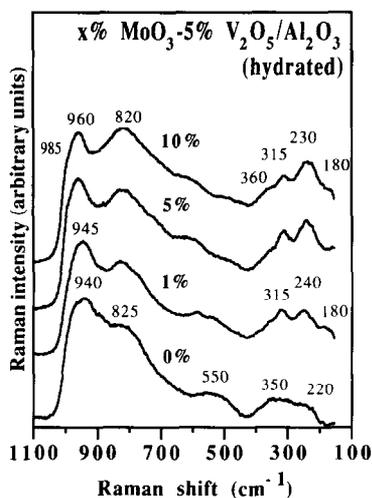


Fig. 1. Raman spectra of $x\% \text{MoO}_3\text{-}5\% \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ under ambient conditions. The molybdenum oxide loading, x , increases from 0% to 10%.

Fig. 2. Raman spectra of $5\% \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $5\% \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, and $5\% \text{Fe}_2\text{O}_3\text{-}5\% \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ under ambient conditions.

of hydrated decavanadate species (bands at ≈ 985 (shoulder), 820, 315, ≈ 230 and $\approx 180 \text{ cm}^{-1}$) [31, 32] and octahedrally coordinated polymolybdate (bands at 960, ≈ 360 , $\approx 230 \text{ cm}^{-1}$) [12, 34].

Comparison of the Raman spectra of the single $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ [31, 32] and $\text{MoO}_3/\text{Al}_2\text{O}_3$ systems [12, 34] with those of the mixed samples shows that the hydrated metavanadate species are converted into hydrated decavanadate species, while the hydrated MoO_4^{2-} species are converted into hydrated $\text{Mo}_7\text{O}_{24}^{6-}$ or $\text{Mo}_8\text{O}_{26}^{4-}$ species, when both metal oxides are present on the alumina support. These observed changes in structure occur because under ambient conditions the metal oxide structures are dependent on the net surface pH at pzc, as discussed above [32]. The presence of both metal oxides decreases the net pH at pzc relative to the individual metal oxide systems. This results in the simultaneous transformation of both vanadium oxide and molybdenum oxide to more polymerized and complex structures. Recently, the same results have been obtained for mixed $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts [30].

$\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5/\text{Al}_2\text{O}_3$

The Raman spectrum of the mixed $5\% \text{Fe}_2\text{O}_3\text{-}5\% \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample under ambient conditions is presented in Fig. 2 together with the Raman spectra of the $5\% \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $5\% \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples. The Raman spectrum of the $5\% \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample shows weak bands at ≈ 615 , ≈ 500 , 410 and $\approx 300 \text{ cm}^{-1}$, which are assigned to crystalline $\alpha\text{-Fe}_2\text{O}_3$ [51]. Raman spectroscopy is very sensitive to the presence of crystalline metal oxide particles, owing to the high cross-section compared with those of surface

metal oxide species. Thus the weak bands of crystalline $\alpha\text{-Fe}_2\text{O}_3$ show that only a small amount of the iron oxide is present as crystalline particles at this surface coverage. The broad band at $\approx 750\text{ cm}^{-1}$ is assigned to a surface iron oxide phase (for further discussion see the dehydrated conditions section).

The presence of both iron oxide and vanadium oxide on the alumina surface yields a different Raman spectrum than observed for the single metal oxide samples. The 940 cm^{-1} band is present as a shoulder, and additional bands are observed at 885 , ≈ 800 , ≈ 500 , ≈ 350 and $\approx 240\text{ cm}^{-1}$. The shift of the V–O stretching mode to lower wavenumber indicates that part of the hydrated metavanadate species is converted into hydrated pyrovanadate ($\text{V}_2\text{O}_7^{4-}$) and hydrated orthovanadate (VO_4^{3-}) species, since pyrovanadate and orthovanadate possess their symmetrical stretching modes at 870 and $\approx 820\text{ cm}^{-1}$, respectively [31, 32]. The weak bands of supported iron oxide are overshadowed by the bands of the supported vanadium oxide species, most probably because the cross section of the former is smaller. The Raman spectra further reveal that iron vanadate, FeVO_4 , is not formed on the alumina surface, since this compound exhibits many intense Raman bands, at $960(\text{m})$, $930(\text{s})$, $890(\text{s})$, $840(\text{s})$, $760(\text{w})$, $730(\text{s})$, $650(\text{w})$, $450(\text{w})$, $370(\text{w})$, $320(\text{w})\text{ cm}^{-1}$ [52].

The transformation of hydrated metavanadate species into hydrated pyrovanadate and orthovanadate species by the presence of iron oxide points to an increase in the net pH at pzc, since pyrovanadate and orthovanadate species are stable only in a basic environment [31, 32, 50]. The increase in the net pH at pzc by the presence of iron oxide occurs since an aqueous solution of iron(III) oxide is basic at low concentrations [50]. A similar effect has recently been reported for hydrated $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts contaminated with alkaline impurities [Na, K] [23, 31].

Dehydrated conditions

$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{Al}_2\text{O}_3$

The Raman spectra of the single $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{Al}_2\text{O}_3$ systems under dehydrated conditions have been reported in previous studies [42] and the results are summarized below. Different surface vanadium oxide and molybdenum oxide species are found on the corresponding dehydrated alumina surfaces, and their ratio is a function of the surface coverages. A highly distorted vanadium oxide species is observed at all vanadium loadings and has been identified as an isolated vanadate species possessing one short terminal V=O bond and three binding V–O–Al bonds [27–29, 33, 35, 36, 38–42, 45]. A second surface species becomes more abundant with increasing vanadium oxide coverage and possesses a moderately distorted structure with more than one short terminal V=O bond (two or three) [28, 33, 38, 40–42, 45]. This second surface vanadium oxide species becomes more polymerized at higher surface coverage, as revealed by additional Raman bands that are characteristic of V–O–V linkages.

For the $\text{MoO}_3/\text{Al}_2\text{O}_3$ system, a surface molybdate species has been observed at all loadings that has been identified as a highly distorted mono-

oxo (one short Mo=O bond) molybdate species with an octahedral coordination of the Mo⁶⁺ cation [34, 42, 44]. A second surface molybdate species is observed in the 5% MoO₃/Al₂O₃ samples, and it has been argued that this species possesses a regular tetrahedral coordination of the Mo⁶⁺ cation [42, 44]. At higher loadings ($\geq 10\%$), a polymolybdate surface species is present on the dehydrated alumina surface. The Raman bands match those of crystalline (NH₄)₆Mo₇O₂₄ or (NH₄)₄Mo₈O₂₆ and are accordingly assigned to octahedrally coordinated molybdate clusters [42].

MoO₃-V₂O₅/Al₂O₃

Figure 3 shows the Raman spectra of the mixed $x\%$ MoO₃-5% V₂O₅/Al₂O₃ samples (with $x=0-10\%$) under dehydrated conditions. The spectrum of the 5% V₂O₅/Al₂O₃ sample reveals the presence of a highly distorted O₃V=O species (sharp band at 1025 cm⁻¹) and a moderately distorted vanadium oxide species with more than one terminal V=O bond (band at 890 cm⁻¹ together with shoulder at ≈ 845 cm⁻¹) [27, 28, 38, 40-42, 45]. In the presence of 1% MoO₃, the Raman band of a highly distorted octahedrally coordinated molybdenum oxide with one short Mo=O bond shows up at ≈ 1000 cm⁻¹ (shoulder), while the broad 890 cm⁻¹ band of the moderately distorted vanadium oxide species becomes more pronounced. The *in situ* Raman spectra of the 5% V₂O₅-5% MoO₃/Al₂O₃ and 5% V₂O₅-10% MoO₃/Al₂O₃ samples reveal the same; however, the sharp band of the highly distorted vanadium oxide species (≈ 1025 cm⁻¹) is now present as a shoulder on the 1000 cm⁻¹ band of the highly distorted molybdenum oxide species.

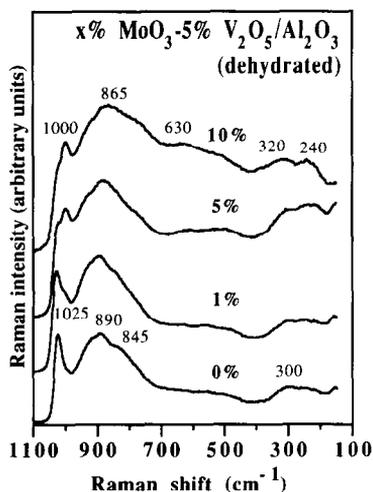


Fig. 3. Raman spectra of $x\%$ MoO₃-5% V₂O₅/Al₂O₃ under dehydrated conditions. The molybdenum oxide loading, x , increases from 0% to 10%.

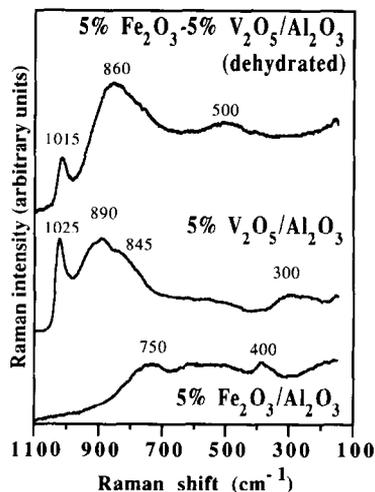


Fig. 4. Raman spectra of 5% Fe₂O₃/Al₂O₃, 5% V₂O₅/Al₂O₃, and 5% Fe₂O₃-5% V₂O₅/Al₂O₃ under dehydrated conditions.

The most important observation for this series of mixed samples under dehydrated conditions is that the band in the 800–900 cm^{-1} region increases with increasing molybdenum oxide loading. The increase in intensity of this broad band is larger than the cumulative contributions of the broad bands observed in the *in situ* Raman spectra of the individual systems [42]. An increase in the broad 800–900 cm^{-1} band has also been observed in the single-component $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{Al}_2\text{O}_3$ systems with increasing surface coverage [42]. Thus the presence of both molybdenum and vanadium oxide on the dehydrated alumina surface has the same effect on the metal oxide surface structures as increasing the surface coverage in the single-component systems. This is in agreement with recent IR spectroscopic studies that revealed that molybdenum oxide and vanadium oxide titrate the same type of surface OH_{Al} groups as a function of the surface coverage [53]. Addition of both metal oxides to the alumina results in competition for the same surface hydroxyl groups, comparable with increasing the surface coverage. Recently, a similar effect has been observed for the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ system, where the presence of tungsten oxide also results in an enhancement of the relative concentration of the moderately distorted vanadium oxide species under dehydrated conditions [30].

$\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5/\text{Al}_2\text{O}_3$

Figure 4 shows the Raman spectrum of the 5% $\text{Fe}_2\text{O}_3\text{--}5\%$ $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample together with the Raman spectra of the 5% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and 5% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples under dehydrated conditions. The spectrum of the 5% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample has been discussed above, while the spectrum of the 5% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample is nearly identical with the Raman spectrum recorded under ambient conditions (see Fig. 2). The slightly decreased intensity of the bands of crystalline $\alpha\text{-Fe}_2\text{O}_3$ (613, 500, 410, 297 and 220 cm^{-1}) under dehydrated conditions is most probably due to the heterogeneous character of the catalyst surface. Under ambient conditions the sample is spun at 2000 rpm, yielding an averaged Raman spectrum, while under dehydrated conditions the sample is stationary and only a small part of the surface with the size of the laserbeam is illuminated. The broad band at ≈ 750 cm^{-1} does not match the Raman bands of bulk iron oxide such as $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$ (550, 474, 414, 397, 298 cm^{-1}), $\gamma\text{-FeOOH}$ (380, 252 cm^{-1}), FeO (663, 616 cm^{-1}) or Fe_3O_4 (663, 616 cm^{-1}) [51]. This demonstrates that the state of the iron oxide species possessing the 750 cm^{-1} band is very different from that found in these crystallites. This iron oxide species is also very different from supported metal oxide with a higher oxidation state (Re^{7+} , W^{6+} , Mo^{6+} , Cr^{6+} , V^{5+} , Nb^{5+}). These metal oxides exhibit strong bands in the 900–1000 cm^{-1} region, which are indicative of terminal $\text{M}=\text{O}$ bonds. These bands sharpen and shift to higher frequency upon dehydration, and it has been concluded that these metal oxides are located on the support surface [37, 42]. The supported iron oxide band at ≈ 750 cm^{-1} indicates that only $\text{Fe}\text{--O}$ bonds are present, and the insensitivity of this band to the removal of moisture suggests that water molecules do not coordinate to this supported iron oxide

phase. Both the presence of Fe–O bonds and the water insensitivity are consistent with the incorporation of the iron oxide into the defects of the Al_2O_3 surface. This assignment is supported by recent Mössbauer spectroscopy investigations that detected Fe^{3+} in solid solution in the alumina support [46–48].

The broad band of the moderately distorted vanadium oxide species in the $800\text{--}900\text{ cm}^{-1}$ region becomes very intense in the presence of iron oxide, while the sharp band of the $\text{O}_3\text{V}=\text{O}$ species is shifted down from 1025 to 1015 cm^{-1} . This indicates that the relative amount of the highly distorted $\text{O}_3\text{V}=\text{O}$ species has decreased, since it has been observed that this band shifts from 1025 to 1015 cm^{-1} with decreasing vanadium oxide loading in the single $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system [42]. Both the enhanced intensity of the broad $800\text{--}900\text{ cm}^{-1}$ band and the shift of the sharp band to 1015 cm^{-1} indicate that the presence of iron oxide promotes the formation of the moderately distorted vanadium oxide species under dehydrated conditions.

Thus addition of molybdenum oxide and iron oxide to the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system have similar effects on the molecular structure of the surface vanadium oxide species. The molybdenum oxide and vanadium oxide species are both present on the alumina surface and compete for the same hydroxyl groups, as discussed above. The iron oxide species are most probably adsorbed into the alumina surface, since they are not influenced by the presence of moisture. It is, therefore, not clear yet how these iron oxide species can influence the surface structure of vanadium oxide species that are located on the alumina surface. The same results have also recently been obtained by adding nickel oxide or cobalt oxide to the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system [52].

Conclusions

The presence of both vanadium oxide and molybdenum oxide on the hydrated alumina surface results in the conversion of the hydrated metavanadate species into hydrated decavanadate species and the conversion of the hydrated MoO_4 species into hydrated octahedrally coordinated clusters. This is due to the decrease in the net pH at pzc relative to the individual metal oxide systems, as described by the model of Deo and Wachs. For the mixed $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample, it has been found that the hydrated metavanadate species are converted into hydrated pyrovanadate and orthovanadate species, which is ascribed to the basic nature of the surface iron oxide species at low loadings.

The presence of both vanadium oxide and molybdenum oxide on the dehydrated alumina surface results in increased concentrations of surface vanadate and molybdate species, which are found at much higher surface coverage in the corresponding individual metal oxide systems. These changes in dehydrated surface structures do not occur by a change in the surface pH, as under ambient conditions, since the surface pH can exert its influence only via an aqueous environment. The observed changes are most probably

caused by competition of vanadium oxide and molybdenum oxide species for titrating the same type of alumina hydroxyl groups. A similar effect has been observed in the presence of iron oxide, which also promotes the formation of the moderately distorted vanadium oxide species under dehydrated conditions.

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