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Monolayer V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts prepared by different methods

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Abstract

Two series of supported V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts were synthesized using different preparation methods to determine the possible influence of the preparation procedures upon the final molecular structures of the catalysts. It has been found by means of ambient and in situ Raman spectroscopy that all the employed preparation methods lead to the same types of surface metal oxide species on the titania support. The hydrated surface metal oxide species of both series of the catalysts undergo, after heating in flowing dry air, reversible conversion into the dehydrated analogues. The preparation methods appear to have no influence on the final surface metal oxide structures, but can affect (delay) the process of their formation, as in the case of dry impregnation (thermal spreading) of the V_2O_5/TiO_2 system, due to the thermodynamic and diffusion factors involved.

Keywords: vanadia/titania, molybdena/titania, Raman spectroscopy.

INTRODUCTION

The V_2O_5/TiO_2 system is a subject of considerable interest because of its widespread applications as a catalyst in many important industrial oxidation processes and because it represents a model system for the analysis of interactions at the metal oxide/support interface. Results of many recent studies indicate that the supported V_2O_5/TiO_2 (anatase) is a superior catalyst to unsupported crystalline V_2O_5 for the selective oxidation of hydrocarbons [1–14]. The two-dimensional overlayers of surface vanadium oxide species on the titania support were found to be the active phase for these partial oxidation

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reactions and to possess a higher activity and selectivity than crystalline V_2O_5. In addition, the TiO_2 (anatase) support must be covered by a complete monolayer of the surface vanadium oxide species since exposed titania sites are responsible for undesired combustion of the partial oxidation products (especially during *o*-xylene oxidation to phthalic anhydride).

Supported molybdenum oxide catalysts are widely used for hydrodesulfurization and hydrocracking as well as for metathesis of alkenes in the petroleum industry. Recently, they were found to show catalytic activities for the partial oxidation of aliphatic alcohols [15,16]. Similar to supported V_2O_5/TiO_2 catalysts, the two-dimensional overlayers of surface molybdenum oxide species on the titania support were found to be the active sites for partial oxidation and possess a higher activity and selectivity than crystalline MoO_3 [17].

Many different synthesis methods have been used in the preparation of supported metal oxide catalysts because the state of dispersion of the supported metal oxide component plays a critical role in catalytic reactions. In the case of supported V_2O_5/TiO_2 catalysts, catalysts have been prepared by vapour phase grafting with $VOCl_3$ [18,19], non-aqueous impregnation (vanadium alkoxides [20] and vanadium acetate [9]), aqueous impregnation (vanadium oxalate [11]), as well as dry impregnation with crystalline V_2O_5 (spontaneous spreading) [21]. Commercial preparations usually employ aqueous impregnation with vanadium oxalate because of its high solubility and simplicity, but some authors have argued that V_2O_5/TiO_2 catalysts synthesized by vapour phase grafting of $VOCl_3$ result in superior catalytic properties [18]. Similarly, supported MoO_3/TiO_2 catalysts have also been prepared by coprecipitation [22,23], incipient wetness impregnation [24,25], grafting with $MoOCl_4$ [26], by the equilibrium adsorption method [17,27], as well as by spreading [28,29].

The aim of the present work is to investigate the influence of the synthesis method upon the surface structures of V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts. Diverse synthesis methods have been chosen in order to prepare samples with different initial dispersions of supported vanadium and molybdenum oxides ranging from the preparation of molecularly dispersed metal oxides by grafting to the formation of monolayers by heating heterogeneous physical mixtures of V_2O_5/TiO_2 or MoO_3/TiO_2. Two different titania supports were used: commercial titania (Degussa, P-25) and anatase prepared by the hydrolysis of $TiCl_4$. After calcination the catalysts were characterized by Raman spectroscopy to determine the molecular structures of the supported metal oxide components under ambient conditions as well as in situ conditions (elevated temperatures in flowing dry air).

EXPERIMENTAL

Two types of titania supports were used in the present investigation. The first was commercial titania (Degussa P-25, surface area 50 m^2/g, and anatase–rutile ratio ca. 2). The second titania was prepared by hydrolysis of a $TiCl_4$ solution in water with ammonia (1:1), subsequent drying at 120°C for 24 h and calcining at 530°C for 50 h (surface area 46 m^2/g; pure anatase). The latter is denoted henceforth as A46.

Five different supported V_2O_5 on titania samples were prepared by: (1) aqueous impregnation with vanadium oxalate on anatase A46 followed by drying at 120°C for 16 h and calcining at 400 or 450°C for 20 h (vanadia content 4.4 and 6.4 wt.-%, respectively); (2) incipient wetness impregnation with $VO(OC_2H_6)_3$ in ethanol on Degussa P-25 and subsequent drying at 120°C for 16 h and calcining at 450°C for 2 h (vanadia content 4.0 wt.-%); (3) grafting with $VOCl_3$ in n-hexane on anatase A46 followed by the evaporation of the solvent, drying at 120°C for 16 h, and calcining at 400°C for 20 h (V_2O_5 content 4.4 wt.-%); (4) equilibrium adsorption with an ammonium metavanadate as a precursor (aqueous solution with pH = 7.07) on Degussa P-25, drying at 100°C for 24 h and calcining at 500°C for 24 h (V_2O_5 content ca. 4.0 wt.-%); and (5) dry impregnation (thermal spreading) performed by heating of a V_2O_5/anatase A46 physical mixture in air at 500°C for 48 h (V_2O_5 content 4.6 wt.-%). The amount of V_2O_5 deposited on titania was below the monolayer coverage for all the prepared samples which corresponds to ca. 5.5 and ca. 6.0 wt.-% V_2O_5 for anatase A46 and Degussa P-25, respectively. These monolayer values were experimentally obtained by determining the amount of V_2O_5 necessary to form a complete monolayer which is equal to 0.12 wt.-% V_2O_5 per m^2 of the support [19,30].

Five different samples of supported molybdenum oxide on TiO_2 catalysts were prepared by: (1) aqueous impregnation with molybdenum oxalate on the anatase A46; (2) grafting with $MoCl_5$ in $CHCl_3$ on the anatase A46 (both samples were dried at 120°C for 16 h and calcined at 400°C for 24 h; (3) dry impregnation (thermal spreading) with crystalline MoO_3 on A46 performed by heating the MoO_3/anatase A46 physical mixture in air at 450°C for 100 h; (4) aqueous impregnation with ammonium heptamolybdate on Degussa P-25, drying at 120°C for 16 h and calcining at 450°C for 2 h; and (5) the equilibrium adsorption method [17] from an ammonium heptamolybdate aqueous solution at pH = 7.28 on Degussa P-25 and subsequent drying at 100°C for 24 h and calcining at 500°C for 24 h. The amount of MoO_3 deposited on the titania support in the sample prepared by the equilibrium adsorption method was 4.1 wt.-% and for all the other samples the MoO_3 content was equal to 4.0 wt.-%. Similar to V_2O_5, the MoO_3 content was below the monolayer coverage which *essentially corresponds to the same values found for* V_2O_5/TiO_2 *and equals ca.* 0.12 wt.-% MoO_3 per m^2 of the support [17].

The Raman spectra recorded under ambient conditions at room temperature were obtained with a Spectra-Physics Ar^+ laser (Model 171) by utilizing about 10–40 mW of the 514.5 nm line for excitation. About 10–20 mg of each sample was pressed into a thin wafer of about 1 mm thickness with a KBr backing for support. Each sample was then mounted onto a spinning sample holder and rotated at ca. 2000 rpm to avoid local heating effects. The laser beam was focused on a rotating pellet and the scattered radiation from the sample was directed into a Spex Triplemate Spectrometer (Model 1877), where it first passed through the spectrometer's filter stage to filter out the elastic and pseudo-elastic components and then through the spectrograph stage where the light was spatially dispersed, as a function of frequency, and finally projected onto the focal plane of the intensified photodiode array of the detector. The pixel elements of the photodiode array (ca. 1000 intensified elements) were quickly scanned with an optical multichannel analyzer (OMA III: EG&G, Princeton Applied Research, Model 1463). The photodiode array was thermoelectrically cooled to $-35\,^{\circ}$C. The Raman spectra were recorded and processed using an OMA III (PAR) dedicated computer software package. The spectral resolution and reproducibility was experimentally determined to be better than 2 cm^{-1} (1200 grooves/mm in the spectrograph stage).

The in situ Raman spectra were collected in a similar instrumental configuration. Each sample consisted of ca. 200–300 mg of pure catalyst and was pressed into a thin wafer of about 2 mm. The wafer was placed into a stationary sample holder that was installed in an in situ cell equipped with an atmosphere control unit and an electric heating coil. Both the sample holder and cell were made of quartz. More details on the in situ cell arrangements can be found elsewhere [31]. Oxygen (Linde Ultra High Purity) was introduced into the cell from a manifold at a rate of 100–200 cm^3 min^{-1} with a delivery pressure of 150–200 Torr. The combination of a detector containing ca. 700 intensified pixel elements and a grating of 1800 grooves/mm in the spectrograph stage provided a higher resolution of the recorded spectra (experimentally determined to be better than 1 cm^{-1}). Three spectra were recorded for each sample: at room temperature under ambient air, in flowing dry air at 450°C, and near room temperature (50°C) after cooling.

All the Raman spectra were recorded in the 800–1100 cm^{-1} range because of the strong titania Raman bands below 800 cm^{-1} which prevent the detection of the additional bands of the supported vanadium and molybdenum oxide phases.

RESULTS

The Raman spectra of the V_2O_5/TiO_2 catalysts prepared by the different synthesis methods are shown in Fig. 1. The spectra were obtained under ambient conditions where the oxide surfaces are known to be hydrated [31,32]. The amount of V_2O_5 dispersed onto titania is below the monolayer coverage for all the studied samples. The nature of the supported vanadium oxide phase is determined by comparing the Raman spectra of the supported vanadium oxide sample with the spectra of vanadium oxide reference compounds [33,34].

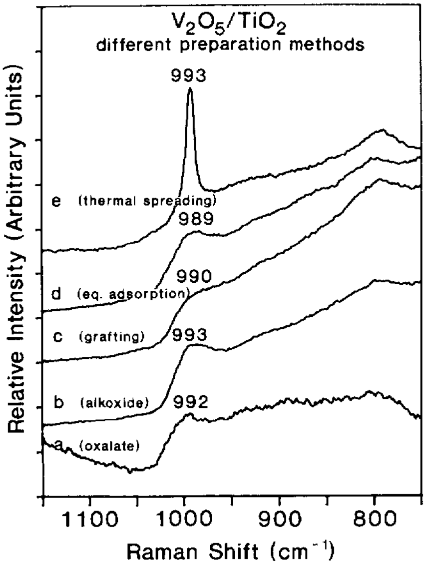

Fig. 1. Raman spectra of V_2O_5/TiO_2 catalysts prepared by different methods: (a) aqueous impregnation with vanadium oxalate; (b) incipient wetness impregnation with vanadium isopropoxide; (c) grafting with $VOCl_3$ in n-hexane; (d) equilibrium adsorption from ammonium metavanadate aqueous solution at pH = 7.07; (e) dry impregnation (thermal spreading) from a V_2O_5/TiO_2 (A46) physical mixture. The V_2O_5 content and calcination temperature are given in the experimental section.

The Raman spectra exhibit two bands at 790 cm^{-1} and 990 cm^{-1}. The weak band at about 790 cm^{-1} is due to the first overtone of the 395 cm^{-1} band of TiO_2 (anatase). As the titania support does not possess any Raman bands between 800 and 1100 cm^{-1}, the broad band at about 990 cm^{-1} is due to the surface vanadium oxide phase on the titania support. Comparison with recent solid state ^{51}V NMR results leads to the conclusion that the 990 cm^{-1} band originates from octahedrally coordinated surface vanadia species [35]. The Raman spectra and NMR results corresponding to the 990 cm^{-1} band match the distorted octahedral vanadia species present in decavanadate clusters ($V_{10}O_{28}^{6-}$) best [35]. The Raman spectra (a, b, c, d) presented in Fig. 1 do not exhibit a sharp band at 994 cm^{-1} which is characteristic of pure crystalline V_2O_5. Thus, these preparation methods form a surface vanadium oxide overlayer possessing essentially the same molecular structure.

There is, however, a difference between the preparation methods with respect to the kinetics of the vanadia overlayer formation. The Raman spectra of the V_2O_5/TiO_2 catalysts, prepared by impregnation with vanadium oxalate on anatase A46 as a function of V_2O_5 content and the calcination temperature, are presented in Fig. 2. Two different amounts of V_2O_5 were deposited on anatase A46: below monolayer coverage (4.4 wt.-%) and slightly above mono-

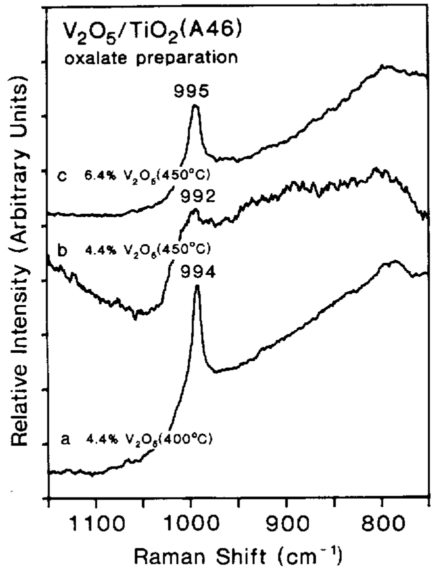

Fig. 2. Raman spectra of V_2O_5/TiO_2 (A46) catalysts prepared by aqueous impregnation with vanadium oxalate as a function of V_2O_5 content and the calcination temperature (T_c): (a) 4.4 wt.-% V_2O_5, $T_c = 400°C$; (b) 4.4 wt.-% V_2O_5, $T_c = 450°C$; (c) 6.4 wt.-% V_2O_5, $T_c = 450°C$. All the samples were calcined for 20 h.

layer coverage (6.4 wt.-%). The preparation of the V_2O_5/TiO_2 catalyst by the grafting method results in a well dispersed vanadia phase already at 400°C (Fig. 1c), whereas the impregnated sample must be calcined at a higher temperature to reach the same state of vanadia dispersion (Fig. 2a and b). The impregnation with vanadium oxalate was performed by evaporation of the titania suspension in an aqueous vanadium oxalate solution which apparently resulted in the formation of vanadia oxalate clusters which decomposed, after calcining, into V_2O_5 crystallites. In order to completely disperse the V_2O_5 crystallites on titania into a surface phase a higher calcination temperature than that of the grafted sample was required. Thus, the Raman spectrum of the 4.4 wt.-% V_2O_5/anatase A46 sample calcined at 400°C (Fig. 2a) exhibits the sharp 994 cm^{-1} band characteristic of crystalline V_2O_5. Increasing the calcination temperature to 450°C brings about the disappearance of the sharp 994 cm^{-1} band and the appearance of the broad 992 cm^{-1} band which is characteristic of the surface vanadium oxide overlayer on titania. Thus, additional heating is apparently required to completely convert the crystalline V_2O_5 phase into the surface vanadium oxide phase for samples containing less than a monolayer. In the Raman spectrum of the V_2O_5/anatase A46 sample containing a V_2O_5 amount exceeding monolayer coverage (6.4 wt.-%), the sharp 995 cm^{-1} band is still visible even after heating at 450°C (Fig. 2c). It is consistent with previous findings that V_2O_5 in excess of the monolayer coverage on titania is converted into crystalline V_2O_5 which remains unchanged even upon additional heating [11]. The influence of the initial dispersion of V_2O_5 on the formation kinetics of the vanadium oxide overlayer is seen better in the case of the 4.6 wt.-% V_2O_5/anatase A46 prepared from the physical mixture. The Raman spectrum of such a mixture calcined at 500°C for 48 h still exhibits the sharp 993 cm^{-1} band which is characteristic of crystalline V_2O_5 (Fig. 1e), and which almost completely screens the broad 990 cm^{-1} band originating from the dispersed vanadia (cf. Fig. 4). The significantly stronger Raman scattering from crystalline V_2O_5 relative to the surface vanadium oxide species suggests that the crystalline V_2O_5 component may only account for a small fraction of the supported vanadium oxide in the catalyst. The results presented above show, with the exception of the dry impregnation method which requires more extensive calcination times, that the method of synthesis of supported vanadium oxide catalysts is not critical for the preparation of surface vanadium oxide phases (monolayer-type catalysts) since all the preparations yield the same surface vanadium oxide overlayer on the titania support.

The in situ Raman spectra of the V_2O_5/TiO_2 sample prepared by impregnation with vanadium oxalate on anatase A46 is presented in Fig. 3. The ambient Raman spectrum of the hydrated surface is shown in Fig. 3 for comparison since the laser beam induced the dehydration of the hydrated vanadia species even at ambient temperature. It is seen that the 992 cm^{-1} band, characteristic of the hydrated surface vanadia species on titania, shifts to higher frequencies after dehydration brought about by the laser beam or high tem-

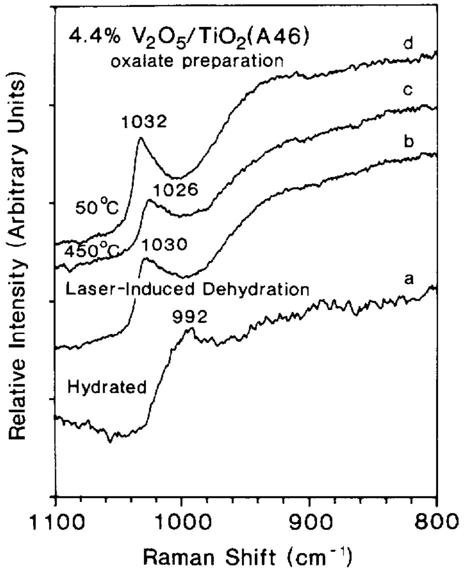

Fig. 3. In situ Raman spectra of V_2O_5/TiO_2 (A46) catalysts prepared by the aqueous impregnation with vanadium oxalate.

peratures. This shift has been interpreted as the change in the coordination of the surface vanadia species from octahedral to tetrahedral upon dehydration as revealed by solid state ^{51}V NMR experiments [35]. The Raman and NMR results corresponding to the 1020–1030 cm^{-1} band suggest a surface tetrahedral structure possessing one short apical V=O bond and three intermediate bridging bonds. At about 940 cm^{-1} an additional broad Raman band is also visible in Fig. 3. The solid state ^{51}V NMR experiments revealed that the 940 cm^{-1} Raman band originates from tetrahedrally coordinated surface vanadia species possessing two terminal and two bridging oxygens [35]. The Raman and NMR results of the surface vanadia species corresponding to the 940 cm^{-1} band match the distorted tetrahedral vanadia species present in linear polymeric metavanadate compounds best. The in situ Raman spectra of the 4.6 wt.-% V_2O_5/anatase A46 physical mixture preheated at 450°C for 5 h are shown in Fig. 4. The 992 cm^{-1} band characteristic of the hydrated vanadium oxide species is hidden by the overlap of the sharp 994 cm^{-1} band of crystalline V_2O_5 since upon heating the band at about 1020–1030 cm^{-1} appears which is characteristic of the dehydrated surface vanadium oxide overlayer. The lower intensity of the 991 cm^{-1} band at 450°C as compared to the room temperature spectra is due to thermal broadening. Note that the sharp 994 cm^{-1} Raman band of crystalline V_2O_5 reappears upon cooling the sample to 50°C which removes the thermal broadening. Identical in situ Raman results were also obtained for the V_2O_5/TiO_2 samples prepared by the other methods and, again,

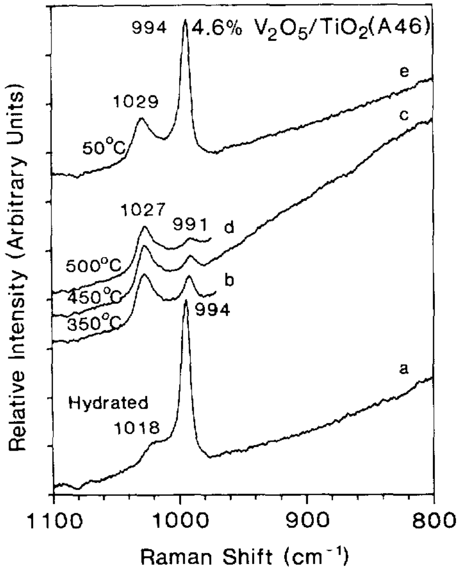

Fig. 4. In situ Raman spectra of the 4.6 wt.-% V_2O_5/anatase A46 physical mixture preheated at 450°C for 5 h.

lead to the conclusion that all the preparations result in the same surface vanadium oxide overlayer on the titania support.

The Raman spectra of the MoO_3/TiO_2 catalysts prepared by different methods are shown in Fig. 5. The weak band at 790 cm^{-1} is due to the first overtone of the 395 cm^{-1} band of TiO_2 (anatase) and the supported molybdenum oxide phase on titania introduced a new Raman feature at about 960 cm^{-1}. This new band has been shown to originate from a hydrated molybdenum oxide overlayer on the titania support and has been assigned to $Mo_7O_{24}^{6-}$ /$Mo_8O_{26}^{4-}$ clusters [24,25,36,37]. The lack of sharp Raman bands due to crystalline MoO_3 at about 816 and 994 cm^{-1} demonstrates that the molybdenum oxide monolayer on titania is easily formed. Even calcination of the 4.0 wt.-% MoO_3/anatase A46 physical mixture at 450°C for 100 h completely converts the crystalline MoO_3 component into a molybdenum oxide overlayer (see Fig. 5e). Thus, the method of synthesis of the supported molybdenum oxide catalyst appears to be of secondary importance both for preparing the molybdenum oxide monolayer as well as for the kinetics of its formation. This is somewhat in contrast to the results for the V_2O_5/TiO_2 system where the synthesis method affects the kinetics of the vanadium oxide monolayer formation.

The in situ Raman spectrum of MoO_3/TiO_2 prepared by aqueous impregnation of molybdenum oxalate onto TiO_2 (A46) is presented in Fig. 6. Upon

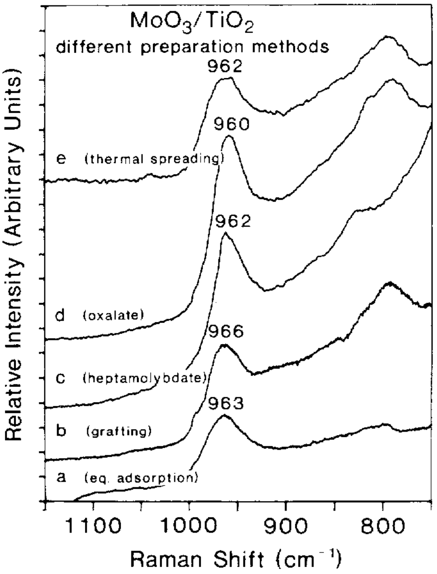

Fig. 5. Raman spectra of MoO_3/TiO_2 catalysts prepared by different methods: (a) equilibrium adsorption from ammonium heptamolybdate aqueous solution at pH = 7.28; (b) grafting with $MoCl_5$ in $CHCl_3$; (c) aqueous impregnation with ammonium heptamolybdate; (d) aqueous impregnation with molybdenum oxalate; (e) dry impregnation (thermal spreading) from a MoO_3/TiO_2 (A46) physical mixture.

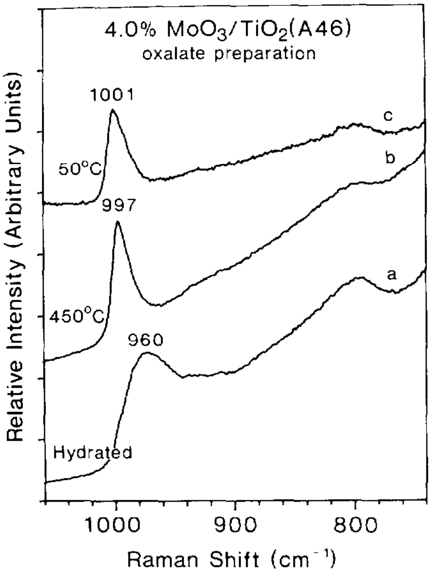

Fig. 6. In situ Raman spectra of MoO_3/TiO_2 (A46) catalyst prepared by aqueous impregnation with molybdenum oxalate.

heating, the 960 cm^{-1} band which is characteristic of the hydrated molybdenum oxide species on titania, shifts to ca. 1000 cm^{-1} due to dehydration of the surface molybdenum oxide overlayer on the titania support [32]. The Raman band at ca. 1000 cm^{-1} has been assigned to a highly distorted MoO_6 octahedral surface species possessing one short apical Mo=O bond, four intermediate bridging bonds, and one very long bridging bond [38]. Identical in situ Raman results were also obtained for the MoO_3/TiO_2 samples prepared by the other synthesis methods and, again, lead to the conclusion that all the preparations result in the same surface molybdenum oxide overlayer on the titania support.

DISCUSSION

The Raman measurements of the supported V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts, under ambient (hydrated) as well as in situ (dehydrated) conditions, reveal that the synthesis method does not influence the molecular structures of the surface vanadium oxide or molybdenum oxide overlayer on the titania support. These observations lead to the conclusion that the final molecular states of the surface metal oxide overlayers are controlled by the thermodynamics of the interactions at the metal oxide–oxide support interface and cannot be modified by the synthesis method. The unusually strong driving force for the formation of the same surface vanadium oxide and molybdenum oxide species is best exemplified by the thermal spreading experiments of the metal oxide physical mixtures. In addition, in situ Raman studies with supported V_2O_5 and MoO_3 catalysts on Al_2O_3, ZrO_2, and Nb_2O_5 supports reveal that the same surface vanadium oxide and molybdenum oxide species are also present on these oxide supports [38]. Thus, it appears that the molecular structures of the dehydrated surface vanadium oxide and molybdenum oxide species are controlled by thermodynamic factors and are independent of the synthesis methods as well as the specific nature of the oxide support (at least for TiO_2, Al_2O_3, ZrO_2, and Nb_2O_5).

The kinetics of formation of the surface metal oxide overlayers, however, depends on the preparation method as well as the surface mobility of the specific metal oxide (i.e. V_2O_5 vs. MoO_3). The two most extreme preparation methods are grafting with monomeric precursors and thermal spreading of physical mixtures of the crystalline metal oxides. In the case of MoO_3/TiO_2, both synthesis methods resulted in a complete dispersion of the molybdenum oxide component over the titania support and the absence of crystalline MoO_3. Thus, the surface mobility of molybdenum oxide appears to be rather high in the 400–450°C temperature range and all preparation methods, even physical mixtures, will yield the same result after moderate heating. In the case of V_2O_5/TiO_2, however, the extreme synthesis methods of grafting and thermal spreading of the physical mixtures of the crystalline metal oxides yielded slightly different results. The grafting approach resulted in the complete dispersion of the vanadium oxide component over the titania support and the absence of crystalline V_2O_5, while the thermal spreading of the V_2O_5/TiO_2 physical mixture resulted in the incomplete dispersion of the vanadium oxide component and the presence of residual crystalline V_2O_5. Clearly, the surface mobility of vanadium oxide seems to be lower than molybdenum oxide in the 400–450°C temperature range and longer calcination times and higher calcination temperatures are required to completely disperse the vanadium oxide over the titania support. Thus, the formation kinetics of the surface molybdenum oxide overlayer is relatively fast and not significantly influenced by the preparation method, whereas the formation kinetics of the surface vanadium oxide overlayer on titania is somewhat more sluggish and is affected by the preparation method (i.e. grafting vs. thermal spreading). Similar kinetic results would be expected on other oxide supports (i.e. Al_2O_3, ZrO_2, and Nb_2O_5) that form surface vanadium oxide and molybdenum oxide overlayers since the surface diffusion rates are intrinsic properties of V_2O_5 and MoO_3.

CONCLUSIONS

A series of supported V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts were prepared by different synthesis methods [grafting, aqueous impregnation, non-aqueous impregnation, equilibrium adsorption and dry impregnation (thermal spreading)] in order to determine the possible influence of the preparation methods upon the final molecular states of the catalysts. The molecular structures of the supported V_2O_5/TiO_2 and MoO_3/TiO_2 catalysts were determined with Raman spectroscopy. The Raman characterization results revealed that all the preparation methods yielded the same surface molybdenum oxide species on TiO_2 and demonstrate that the synthesis method is not critical for the preparation of supported MoO_3/TiO_2 catalysts. The Raman characterization results for V_2O_5/TiO_2 revealed that the same surface vanadium oxide species on TiO_2 was also formed from all the different synthesis methods. However, the amount of residual crystalline V_2O_5 present in the supported V_2O_5/TiO_2 catalyst depended on the specific synthesis method because of the lower surface diffusion rates of vanadium oxide relative to molybdenum oxide. Thus, the final molecular states of the surface vanadium oxide and the molybdenum oxide were independent of the preparation methods and were dictated by thermodynamic factors, whilst the amount of residual crystalline V_2O_5 and MoO_3 depended on the preparation methods as well as the diffusion rates of the specific metal oxides. The vanadium oxalate and heptamolybdate aqueous impregnation methods correspond to the commercial preparations of such catalysts.

The in situ Raman spectroscopy measurements also revealed that the molecular structures of the surface vanadium oxide and the molybdenum oxide overlayers on titania depend on the extent of hydration/dehydration of the catalyst surface. The hydrated titania surfaces possess solvated metal oxide clusters, $V_{10}O_{28}^{6-}$ and $Mo_7O_{24}^{6-}$ /$Mo_8O_{26}^{4-}$, and the dehydrated titania surfaces possess highly distorted surface metal oxide species, VO_4 and MoO_6, respectively. Therefore, the different preparation methods will initially form either the hydrated or dehydrated metal oxide species. The interplay between the different synthesis methods and the hydrated/dehydrated states of the catalyst surface are schematically presented in Fig. 7. For example, thermal spreading is a dry impregnation method performed at elevated temperatures in flowing air and consequently only dehydrated surface metal oxide species result

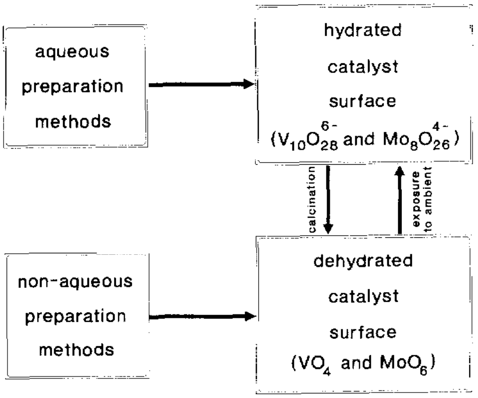

Fig. 7. Relationships between the different synthesis methods and the hydrated/dehydrated states of the catalyst surface.

from this synthesis. However, exposure of the sample to ambient air, which contains moisture, will immediately hydrate the catalyst surface and convert the dehydrated surface metal oxide species to their hydrated analogues. Additional heating in dry air will dehydrate the surface and again form the dehydrated surface metal oxide, species. Aqueous preparation methods, as would be expected, begin with hydrated surface metal oxide species and require heating in dry air to remove the adsorbed moisture to form a dehydrated catalyst surface. Exposure to ambient conditions will hydrate the surface and again form the hydrated surface species. Thus, the preparation method is merely a determinant of the initial state, hydrated or dehydrated, of the catalyst surface since the conversion between the hydrated/dehydrated states of the catalyst surface readily occurs and depends only on the sample environment.

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