

Reaction induced spreading of metal oxides: *in situ* Raman spectroscopic studies during oxidation reactions

Y. Cai^{*,†}, C.-B. Wang[†] and I. E. Wachs[†]

Zettlemoyer Center for Surface Studies and Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA

1. INTRODUCTION

Metal oxides, particularly oxides of vanadium and molybdenum, are widely used as catalysts in numerous industrial applications (oxidation, oxidative dehydrogenation, dehydrogenation, olefin metathesis, olefin polymerization, selective catalytic reduction (SCR) and hydrodesulfurization (HDS)/hydrodenitrogenation (HDN)). In many of the applications, these metal oxides are supported on a high surface area metal oxide substrate, such as Al_2O_3 or TiO_2 , to form an active surface metal oxide species (two-dimensional metal oxide overlayer). These supported metal oxide catalysts are typically prepared by impregnation of the corresponding soluble metal oxide salts, followed by drying and calcination at elevated temperatures (400-600°C). There have been recent reports in the literature that an alternative route to the preparation of such supported metal oxide catalysts involves solid-state reactions, thermal spreading or spontaneous dispersion, of physical mixtures of the pure metal oxides at temperatures of 400-500°C [1-6]. However, no studies have examined the direct influence of the reaction environment on the spreading of metal oxides. In the present investigation, a new phenomenon of reaction induced spreading of crystalline MoO_3 and V_2O_5 on oxide supports is observed at temperatures much lower than that required for thermal spreading via solid-state reactions, 200-250°C vs. 400-500°C.

2. EXPERIMENTAL

The MoO_3 and V_2O_5 crystalline powders were obtained from Aldrich. The TiO_2 support (P-25; 55 m²/g) was purchased from Degussa and the SnO_2 support (3.7 m²/g) from Aldrich. The physical mixtures of the binary oxides were prepared by combining an appropriate amount of MoO_3 (or V_2O_5) with 5.0 g of TiO_2 (or SnO_2) and 150 ml of pentane (Aldrich) in a beaker, and vibrating the mixtures for 15 minutes in an ultrasonic bath. After evaporation of pentane, the samples were dried for 16 hours at 100°C in air. No further treatments were performed.

*Current address: United Catalysts Inc., 1227 South 12th Street, Louisville, KY 40210.

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Thermal spreading was studied by treating the catalysts in an oven at a constant temperature for 1 h. Both loose powder catalysts and samples pressed into self-supporting wafers were investigated in the current studies. After the thermal treatments, Raman spectra of the catalysts were recorded in an ambient environment or in a controlled oxygen atmosphere. In the latter case, the samples were heated in oxygen (Linde Gas, ultra-high purity) in a dehydration cell for 45 minutes at 300 °C and then cooled to about 50 °C to obtain the Raman spectra. Additional details about the Raman spectrometer can be found elsewhere [5].

Reaction induced spreading during alcohol oxidation (methanol, ethanol and 2-butanol) was also investigated with both loose powder catalysts and samples pressed into self-supporting wafers. The self-supporting wafers were investigated with an in situ Raman spectrometer system that allowed monitoring of the changes during the reaction. A 100-200 mg sample disc was placed in the sample holder, which is mounted into a ceramic shaft rotating at 1500 rpm (see reference [7] for additional experimental details). The catalysts were initially heated in an O₂/He = 16/84 stream at 230 °C for 30 minutes before recording the reference spectrum. A reaction gas mixture of CH₃OH/O₂/He = 4/16/80 was subsequently introduced into the in situ cell at a flow rate of 100 ml(STP)/min and the in situ Raman spectra were collected as a function of time. At the end of the reaction experiment, the methanol was removed from the gas stream and the catalyst was reoxidized in the O₂/He stream.

Alcohol oxidation over the loose powder catalysts were conducted in a fixed bed reactor at 230 °C and atmospheric pressure. The details of the reactor system was previously described elsewhere [8]. The catalysts were pretreated in a flow of O₂/He for 15 min prior to oxidation reaction. A reactant stream of CH₃OH/O₂/He = 6/13/81 with a total flow rate of 100 ml/min was used for methanol oxidation. For ethanol and 2-butanol oxidation, a gaseous mixture of O₂/He (13/81; ml/min) containing saturated ethanol or 2-butanol vapor at ambient temperature was introduced into the reactor. Analyses of reactants and products were carried out by an on-line Hewlett Packard 5890B GC. The spent catalysts were also characterized by Raman spectrometer.

3. RESULTS

3.1. Thermal spreading

The ambient Raman spectra of a catalyst pellet containing a 4% MoO₃/TiO₂ physical mixture after being exposed to different thermal treatments in a furnace are shown in Figure 1. The starting physical mixture only exhibited the Raman bands of crystalline MoO₃ (strong bands at about 814 and 990 cm⁻¹) and the TiO₂ support (strong bands below 700 cm⁻¹). After the one-hour 400 °C thermal treatments, in both dry air and wet air, the Raman bands of crystalline MoO₃ predominate and only a trace of hydrated surface molybdenum oxide species is observed (Raman band at 956 cm⁻¹). The Raman band of the surface molybdenum oxide species slightly increased as the temperature of the thermal treatments increased to 500 °C. Comparison of the initial Raman spectrum with the spectrum of the 500 °C thermally treated catalyst pellet showed that most of the molybdenum oxide was still present as MoO₃ crystals and that only a small amount of surface molybdenum oxide species was present. In contrast to the thermal treatments with the catalyst pellet, almost complete dispersion of crystalline MoO₃ was observed after a 500 °C treatment with the 4% MoO₃/TiO₂ catalyst in the loose powder form. Thermal treatment of the loose powder at 400 °C also showed a significant dispersion of crystalline MoO₃ on the titania support. This demonstrates that strong mass transfer limitations exist when the catalyst is in the form of a pellet, but not in the form of the loose powder. However, the design of the current in

situ Raman cell requires that the catalyst be in the form of a pellet and, consequently, the thermally treated pellet is the appropriate reference for the in situ Raman studies. Analogous thermal treatments, in dry as well as wet air, with a catalyst pellet and catalyst powder consisting of a 4% V_2O_5/TiO_2 physical mixture revealed that no thermal dispersion of V_2O_5 occurred for these samples. Thus, thermal treatments of physical mixtures of MoO_3/TiO_2 and V_2O_5/TiO_2 at 400-500°C for 1 hour (1) result in the formation of surface molybdena species, (2) do not result in the formation of surface vanadia species and (3) the concentrations of surface species are significantly enhanced for catalysts in loose powder form compared to catalysts in pellet form.

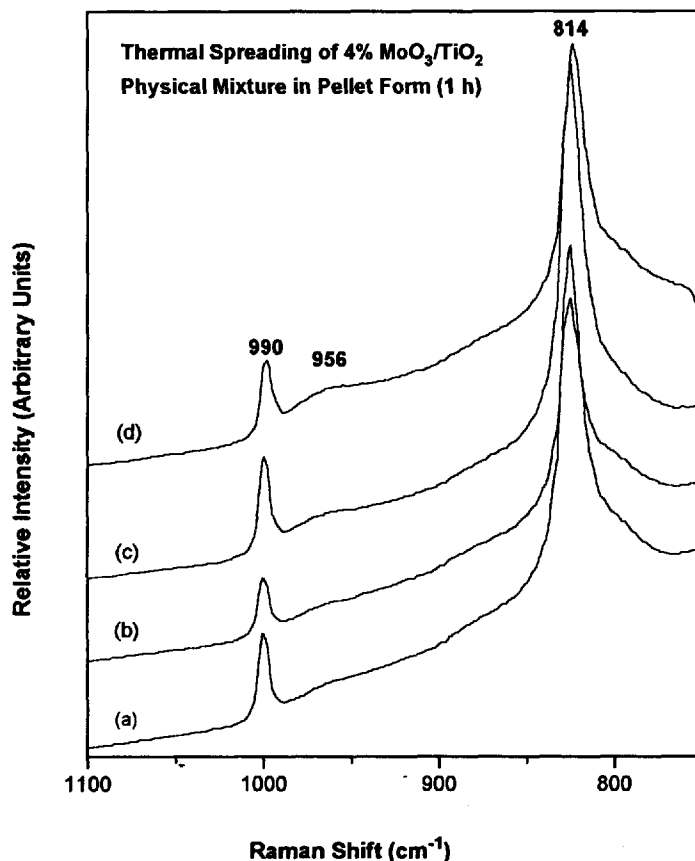


Figure 1. Ambient Raman spectra of physical mixture of 4% MoO_3/TiO_2 catalyst pellet after different thermal treatments: (a) dry air (400°C, 1 h), (b) wet air (400°C, 1 h), (c) dry air (450°C, 1 h) and (d) dry air (500°C, 1 h).

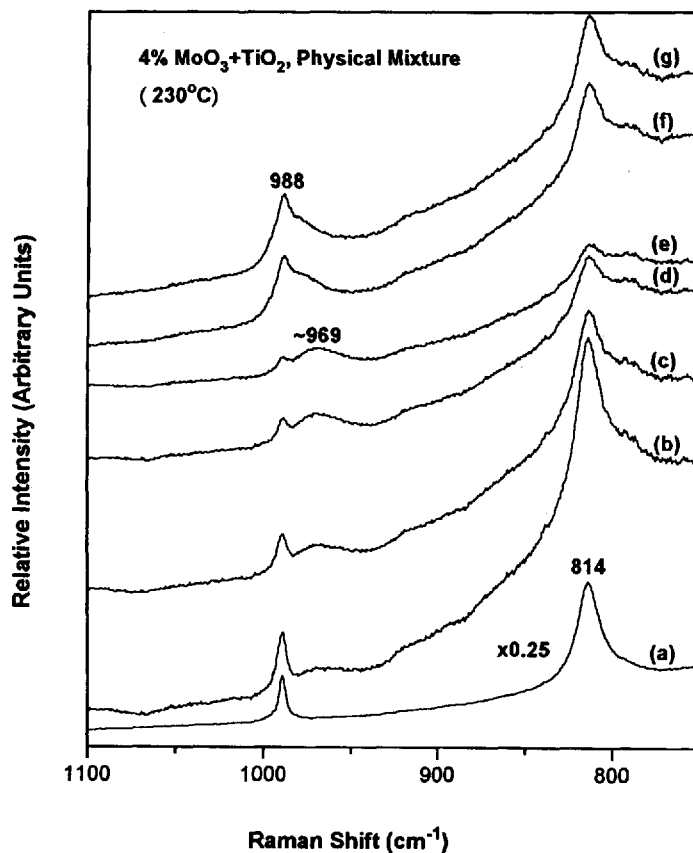


Figure 2. In situ Raman spectra of physical mixture of 4% MoO₃/TiO₂ catalyst pellet during methanol oxidation at 230°C: (a) before methanol oxidation, (b) 20 min, (c) 1 h, (d) 3 h, (e) 5 h, (f) after reaction, oxidation of catalyst for 30 min and (g) after reaction, oxidation of catalyst for 1 h.

3.2. Methanol Oxidation

The in situ Raman spectra of a catalyst pellet consisting of a 4% MoO₃/TiO₂ physical mixture are shown during methanol oxidation at 230°C in Figure 2. The starting sample, Fig. 2a, only possesses the strong Raman bands of crystalline MoO₃ at 814 and 988 cm⁻¹. Upon exposure to methanol oxidation conditions, Fig. 2b-e, the sharp Raman bands due to crystalline MoO₃ slowly diminish with reaction time and a new broad Raman band at 969 cm⁻¹ is formed. The in situ Raman band at 969 cm⁻¹ has previously been assigned to a surface molybdenum oxide coordinated methoxy, CH₃O, species [9]. Upon switching to a flowing oxygen stream in the absence of methanol, Fig. 2f and g, the Raman band at 969 cm⁻¹ shifted to about 990 cm⁻¹ reflecting the decomposition of the surface methoxy-molybdate complex to a dehydrated surface molybdenum oxide species [9]. Simultaneously, there was also an increase in the Raman bands of crystalline MoO₃ due to the oxidation of the partially reduced MoO₃ particles during the methanol oxidation reaction. Raising the reaction temperature to 300°C for about an hour, figure

not shown, resulted in the complete disappearance of the crystalline MoO_3 Raman bands and only the appearance of the Raman bands associated with the surface molybdenum oxide species. Reoxidation of the sample at 300°C also resulted in the appearance of weak crystalline MoO_3 Raman bands revealing that some residual reduced crystallites still remained and that higher temperature treatments are required to completely disperse the MoO_3 crystals on the titania support. Essentially the same MoO_3 dispersion behavior was observed during methanol oxidation with catalyst pellets consisting of 0.5-1% $\text{MoO}_3/\text{SnO}_2$ physical mixtures. Thus, the above in situ Raman studies clearly demonstrate that reaction induced spreading of crystalline MoO_3 readily occurs over oxide supports during methanol oxidation at very mild temperatures, 230°C .

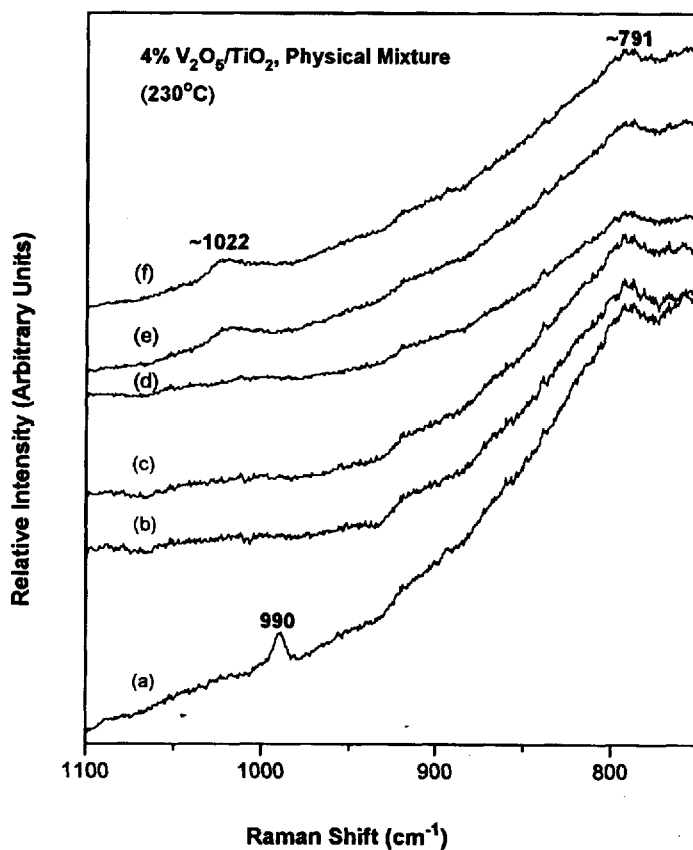


Figure 3. In situ Raman spectra of physical mixture of 4% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst pellet during methanol oxidation at 230°C : (a) before reaction, (b) 30 min, (c) 1 h, (d) 3 h, (e) after reaction, oxidation of catalyst for 30 min, (f) after reaction, oxidation of catalyst for 1 h.

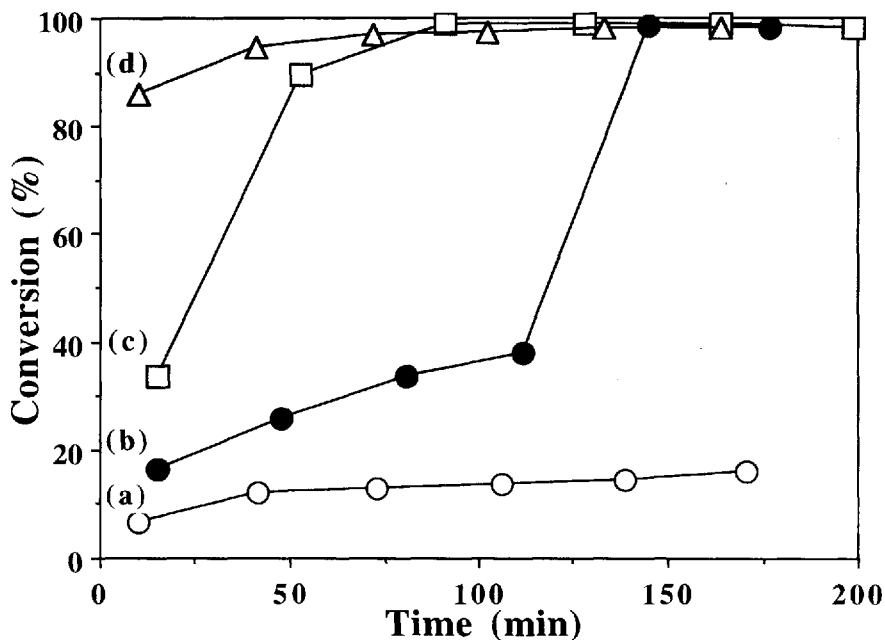


Figure 4. Oxidation of alcohols over catalysts in loose powder form at 230°C as a function of reaction time: (a) methanol oxidation over 4% MoO₃/TiO₂ physical mixture, (b) methanol oxidation over 4% V₂O₅/TiO₂ physical mixture, (c) ethanol oxidation over 4% MoO₃/TiO₂ physical mixture and (d) 2-butanol oxidation over 4% MoO₃/TiO₂ physical mixture.

The in situ Raman spectra of a catalyst pellet consisting of a 4% V₂O₅/TiO₂ physical mixture are shown during methanol oxidation at 230°C in Figure 3. The starting sample, Figure 3a, only exhibits the Raman bands of crystalline V₂O₅ at about 990 cm⁻¹ and the titania support at about 790 cm⁻¹. Exposure of the vanadia-titania catalyst to methanol oxidation at 230°C, Figures 3b-d, completely removes the Raman bands of the V₂O₅ crystals and no new bands due to surface vanadia species are observed. The complete absence of any vanadia Raman bands suggests that the vanadia component of the catalyst was reduced (reduced vanadia gives rise to very weak Raman bands). Reoxidation of the 4% V₂O₅/TiO₂ physical mixture catalyst pellet resulted in the appearance of a new Raman band at 1022 cm⁻¹ associated with surface vanadia species [10,11] and the complete absence of crystalline V₂O₅ particles (no sharp Raman band at about 990 cm⁻¹). Thus, the above in situ Raman studies clearly demonstrate that reaction induced spreading of crystalline V₂O₅ readily occurs over oxide supports during methanol oxidation at very mild temperatures, 230°C.

The catalytic behavior of the above physical mixtures, in loose powder form, were also investigated during methanol oxidation in a fixed-bed reactor as shown in Figure 4a and b. The methanol conversion over 4% MoO₃/TiO₂ continuously increased from about 8 to 16% during the first three hours of reaction. The corresponding methanol oxidation studies over the 4% V₂O₅/TiO₂ catalyst were more dramatic: the methanol conversion continuously increased from about 18 to 37% with reaction time during the first 110 minutes and then exhibited a sharp jump

to 100% methanol conversion at approximately 140 minutes. The jump in methanol conversion was accompanied by an increase in the temperature of the catalyst bed, approximately 244°C, due to the exothermic heat of reaction. Ambient Raman analysis of the spent catalysts revealed that both crystalline MoO_3 and V_2O_5 became almost completely dispersed during the methanol oxidation studies. Additional studies in an oxygen-free methanol environment further demonstrated that the dispersion of the crystalline oxides was not related to the presence of gas phase oxygen. Thus, the increase in methanol conversion as a function of time over $\text{MoO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{TiO}_2$ physical mixtures is directly related to the transformation of crystalline MoO_3 and V_2O_5 into surface molybdena and vanadia species, respectively.

3.3 Ethanol and 2-butanol oxidation

The influence of oxidation reaction environments involving higher alcohols, ethanol and 2-butanol, upon the catalytic behavior and dispersion of MoO_3 on a TiO_2 support was also examined. The catalytic behavior during ethanol and 2-butanol oxidation are shown in Figure 4c and d as a function of reaction time in a fixed-bed reactor containing the catalyst in loose powder form. The higher alcohols were more active than methanol and their conversions increased continuously with reaction time. In the case of ethanol oxidation, some blue Mo deposits were observed on the walls of the reactor exit due to the formation of volatile Mo species. Ambient Raman analysis of the spent catalysts revealed the presence of significant amounts of crystalline MoO_3 as well as the presence of some surface molybdena species. However, the concentrations of the surface molybdena species were much lower than that found after methanol oxidation and the surface molybdena species concentration was greater after ethanol oxidation than 2-butanol oxidation. Thus, these experiments reveal that the dispersion of crystalline MoO_3 particles on TiO_2 supports during oxidation of alcohols follows the trend: methanol > ethanol > 2-butanol.

4. DISCUSSION

The thermal spreading of metal oxides over oxide supports has been intensively investigated over the past decade and much is currently known about this process [1,5]. The driving force for the thermal spreading of metal oxides is related to the lower surface free energy of crystalline oxides such as V_2O_5 and MoO_3 compared to crystalline oxide supports such as TiO_2 , SnO_2 , Al_2O_3 , etc. This process is analogous to the wetting of one solid by another induced by the forces of surface tension in order to lower the surface free energy of the system [2]. The low Tamman temperatures of V_2O_5 and MoO_3 (345 and 397.5°C, respectively) are responsible for the efficient spreading of these metal oxides at temperatures of 400-500°C. Furthermore, the spreading kinetics of the metal oxides are (1) dependent on the structure and morphology of the oxide support, (2) enhanced over well-developed crystal planes and (3) dependent on the specific gaseous environment (oxidizing vs. reducing or wet vs. dry) [5]. Under oxidizing conditions and elevated temperatures, the spreading of crystalline V_2O_5 and MoO_3 is initiated spontaneously at the metal oxide-support interface and subsequent migration occurs by surface diffusion of the metal oxides via vacancies or unoccupied sites in the two-dimensional metal oxide overlayer. Amorphous metal oxide phases are suggested as a transient form between the crystalline metal oxides and the two-dimensional metal oxide overlayers. Moisture enhances the surface diffusion of the metal oxides [1]. Under mildly reducing conditions, the spreading of crystalline metal oxides is significantly retarded due to the much higher Tamman temperatures of the

corresponding reduced crystalline metal oxides [1,5].

The present thermal treatment experiments in air revealed that extensive dispersion of MoO_3 occurred at 400°C and essentially complete dispersion took place at 500°C for the loose powder physical mixture of 4% $\text{MoO}_3/\text{TiO}_2$. In contrast, very little dispersion was observed for comparable thermal treatments for the loose powder physical mixture of 4% $\text{V}_2\text{O}_5/\text{TiO}_2$. The observation that the kinetics of MoO_3 dispersion are faster than the kinetics of V_2O_5 dispersion were also previously observed [12]. The lack of V_2O_5 dispersion by the thermal treatments is somewhat surprising and may be related to the structure and morphology of the titania support employed in the present investigation. The form of the physically mixed metal oxide was also found to significantly affect the dispersion kinetics due to the presence of significant mass transfer limitations in the catalyst pellet relative to the loose powder. The presence of mass transfer limitations in catalyst pellets or wafers typically employed for Raman and IR studies is well-documented in the literature [13]. The present studies demonstrated that significant dispersion of MoO_3 or V_2O_5 on a titania support could not be achieved at temperatures of 500°C with the physically mixed oxides in the form of a catalyst pellet. Thus, dispersion of MoO_3 and V_2O_5 on oxide supports at much lower temperatures for physically mixed catalysts in the form of pellets can not be due to thermal spreading and must occur by another mechanism.

The in situ Raman studies clearly demonstrate that spreading of MoO_3 and V_2O_5 over different oxide supports in the form of catalyst pellets readily occurred during methanol oxidation at temperatures as low as 230°C . Such low temperatures, which are below the Tamman temperatures of these oxides and the temperatures required for thermal spreading in the catalyst pellet (above 500°C), implies that thermal spreading is not involved in the spreading mechanism taking place during methanol oxidation. This suggests that a strong interaction between the gas phase components and the crystalline metal oxide phases may be occurring. Formaldehyde is the major selective oxidation reaction product and is known to interact very weakly with metal oxides such as molybdates and vanadates, and adsorbed formaldehyde is readily displaced by the presence of moisture and methanol [14,15]. Moisture interacts strongly with molybdates [14,15] and vanadates [8], but the thermal spreading experiments did not result in significant dispersion of the crystalline metal oxides in the physically mixed catalyst pellet. The interaction of carbon dioxide with molybdates and vanadates is extremely weak and adsorption is usually not even observed at room temperature [16,17]. In contrast to these gaseous components, the interaction of methanol with molybdates and vanadates is very strong and is much stronger than moisture since adsorption of methanol can displace adsorbed moisture [14,15]. Furthermore, methanol oxidation over crystalline MoO_3 and V_2O_5 results in the deposition of molybdena and vanadia at the exit of the reactor, which possesses lower temperatures [18]. This observation suggests that methanol is able to strongly complex with Mo and V present in crystalline MoO_3 and V_2O_5 to form volatile $\text{Mo}(\text{OCH}_3)_n$ and $\text{V}(\text{OCH}_3)_n$ complexes. The alkoxy complexes of vanadia and molybdena are well known and are liquids at room temperature possessing high vapor pressures. Thus, the low temperature dispersion of metal oxides over oxide supports during methanol oxidation is due to the formation of volatile metal-methoxy complexes that result in vapor phase transport of the oxides. The dispersion mechanism may also occur by surface diffusion of the metal-methoxy complex, but no such information is currently available. The absence of Mo and V deposits at the reactor exit during methanol oxidation suggests that either surface diffusion or readsorption of the volatile M-alkoxides is also taking place. In summary, a new phenomenon of reaction induced spreading of crystalline metal oxides on oxide supports is observed in the present investigation at temperatures much lower than that required for thermal spreading via

solid-state reactions, 200-250°C vs. 400-500°C.

Thermal spreading depends on the Tamman temperature of the crystalline metal oxide phases and reduced metal oxide phases possess very high Tamman temperatures which significantly retard migration [1,5]. However, essentially complete dispersion of V_2O_5 on TiO_2 was observed during methanol oxidation even though the in situ Raman spectra revealed that the vanadia was reduced under the reaction conditions (see Fig. 3). Essentially complete dispersion of MoO_3 on TiO_2 was also observed after treatment of the catalyst in an oxygen-free methanol environment. Thus, the oxidation state of the metal oxide does not appear to influence the kinetics of reaction induced spreading of crystalline metal oxides.

Reaction induced spreading of MoO_3 on oxide supports during oxidation of higher alcohols is significantly reduced relative to methanol oxidation (methanol > ethanol > 2-butanol). The reduced migration kinetics is most probably related to the stability and reactivity of the various alcohols. The rate determining step during the oxidation of alcohols to their corresponding aldehydes or ketones involves breaking the alpha C-H bond of the alkoxides (the carbon bonded to the alkoxy oxygen), and the stability of this bond is related to the number of additional carbon atoms coordinated to the alpha carbon: stability decreases with increasing number of carbon atoms coordinated to the alpha carbon [15,19]. Thus, the methoxy complex is more stable than the ethoxy complex, and the 2-propoxy complex is the least stable among these alkoxy complexes. The greater stability of the Mo-methoxy complex most probably is responsible for the greater volatility and spreading observed during methanol oxidation.

The current findings that reaction induced spreading of metal oxides on oxide supports can occur during oxidation reactions at very low temperatures have important implications for commercial applications as well as fundamental studies. The oxidation of methanol to formaldehyde is industrially conducted with $Fe_2(MoO_4)_3 \cdot MoO_3$ catalysts that contain excess MoO_3 . The strong interaction between methanol and the MoO_3 component results in the stripping of the molybdena from the catalyst and its deposition as MoO_3 crystalline needles at the bottom of the reactor where the temperatures are somewhat cooler. This volatilization phenomenon is responsible for catalyst deactivation (loss of activity and selectivity) and pressure build-up in such commercial reactors [20]. The opposite behavior is observed during methanol oxidation over MoO_3/SiO_2 catalysts at 230°C. The strong interaction of methanol with Mo and the weak interaction between surface molybdena species and the silica support results in agglomeration and crystallization of the surface molybdena species to beta- MoO_3 particles during methanol oxidation [21]. A very important consequence of reaction induced spreading of metal oxides during alcohol oxidation is that the catalyst preparation method of many supported metal oxide systems is not critical since the same surface metal oxide species will form during reaction (especially methanol oxidation) [12,21]. Furthermore, the possibility that reaction induced spreading occurs during oxidation reactions over catalysts composed of physical mixtures needs to be very carefully investigated in such systems before other mechanisms are proposed to account for observed reactivity patterns [22].

5. CONCLUSIONS

A new phenomenon of reaction induced spreading of crystalline MoO_3 and V_2O_5 on oxide supports is observed during methanol oxidation at temperatures much lower than that required for thermal spreading via solid-state reactions, 230°C vs. 400-500°C. The migration of the metal oxides appears to proceed by the formation of volatile $M-(OCH_3)_n$ complexes and is not

influenced by the oxidation state of the metal oxide (both oxidized and reduced metal oxides are readily dispersed). The kinetics of reaction induced spreading of metal oxides during alcohol oxidation is much slower for higher alcohols because of the low stability of the corresponding M-alkoxides compared with the more stable M-methoxides.

REFERENCES

1. H. Knoezinger and E. Taglauer, *Catalysis*, 10 (1993) 1.
2. J. Haber, T. Machej and T. Czeppe, *Surf. Sci.*, 151 (1985) 301.
3. D. Honicke and J. Xu, *J. Phys. Chem.*, 92 (1988) 4699.
4. Y. Xie and T. Tang, *adv. Catal.*, 37 (1990) 1.
5. J. Haber, T. Machej, E. M. Serwicka and I. E. Wachs, *Catal. Lett.*, 32 (1995) 101.
6. F. Cavani, G. Centi, E. Foresti, F. Trifiro and G. Busca, *J. Chem. Soc., Faraday Trans.*, 1, 84 (1988) 237.
7. J.-M. Jehng, H. Hu, X. Gao and I. E. Wachs, *Catal. Today*, 28 (1996) 335.
8. G. Deo and I. E. Wachs, *J. Catal.*, 146 (1994) 323.
9. H. Hu and I. E. Wachs, *J. Phys. Chem.*, 99 (1995) 10911.
10. M. A. Vuurman, I. E. Wachs and A. M. Hirt, *J. Phys. Chem.*, 95 (1991) 9928.
11. G. Went, S. T. Oyama and A. T. Bell, *J. Phys. Chem.*, 94 (1990) 4240.
12. T. Machej, J. Haber, A. M. Turek and I. E. Wachs, *Appl. Catal.*, 70 (1991) 115.
13. Y. Cai and I. E. Wachs, to be published.
14. W.-H. Cheng, *J. Catal.*, 158 (1996) 477.
15. W. Holstein and C. J. Machiels, *J. Catal.*, 162 (1996) 118.
16. K. Segawa and W. K. Hall, *J. Catal.*, 77 (1982) 221.
17. A. M. Turek, I. E. Wachs and E. DeCanio, *J. Phys. Chem.*, 96 (1992) 5000.
18. G. Deo, H. Hu and I. E. Wachs, to be published.
19. W. E. Farneth, R. H. Staley and A. W. Sleight, *J. Am. Chem. Soc.*, 108 (1986) 2327.
20. R. Pearce and W. R. Patterson, *Catalysis and Chemical Processes* (Wiley, New York, 1981) p. 263.
21. M. Banares, H. Hu and I. E. Wachs, *J. Catal.*, 150 (1994) 407.
22. P. Ruiz and B. Delmon, *Catal. Today*, 3 (1988) 199.