Reaction-Induced Spreading of Metal Oxides onto Surfaces of Oxide Supports during Alcohol Oxidation: Phenomenon, Nature, and Mechanisms

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Received June 18, 1998. In Final Form: December 1, 1998

Reaction-induced spreading of bulk metal oxides onto surfaces of oxide supports during alcohol oxidation, a new phenomenon occurring at temperatures much lower than that required for thermal spreading, has been extensively investigated with Raman spectroscopic and fixed-bed catalytic studies. The reaction-induced spreading kinetics were accelerated by reaction of gaseous components with metal oxides to form mobile complex compounds and found to depend on temperature, gaseous component, metal oxide, and oxide support. Increasing the reaction temperature increases the metal oxide spreding rate. The efficiencies of converting three-dimensional bulk metal oxides into two-dimensional surface metal oxide species by different gaseous components are methanol > ethanol > 2-butanol, water > oxygen. The high reaction-induced spreading efficiency of methanol is related to the high volatility and stability of its metal–methoxy complexes. Reaction-induced spreading of CrO3, MoO3, V2O5, Re2O7, and Cr2O3 during alcohol oxidation readily occurs on TiO2 and SnO2 supports but does not take place on SiO2 because of the low interaction energy between SiO2 and surface metal oxide species. Furthermore, reaction-induced spreading does not appear to be influenced by the oxidation state of the spreading metal oxides. The mechanism of reaction-induced spreading proceeds via the reaction of an alcohol with metal cations to form surface mobile and volatile metal–alkoxy complexes and their subsequent transport through surface diffusion and volatilization/readsorption. The reaction-induced spreading of metal oxides is directly reflected in the catalytic properties of such mixed metal oxide materials since the surface metal oxide species are significantly more active than bulk metal oxides for alcohol oxidation reactions. These new findings have important fundamental implications for synergetic effects of metal oxide catalysts composed of physical mixtures and for commercial applications.

Introduction

Surface metal oxide species on oxide supports play a crucial role in the catalytic processes of supported metal oxide catalysts, which have been widely used as catalysts in numerous industrial applications: MoO3/Al2O3 and WO3/TiO2 catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), V2O5/TiO2 catalysts for o-xylene oxidation to phthalic anhydride and selective catalytic reduction (SCR) of NOx. The industrial development of supported metal oxide catalysts over the past five decades has been summarized.

Fundamental molecular structural information about the surface metal oxide species has been obtained by a battery of physical and chemical techniques, including Raman spectroscopy, infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), UV diffuse reflectance spectroscopy (UV-vis), solid-state nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), Mössbauer spectroscopy, surface acidity, adsorption, and probe reactions. The reactivity of the surface metal oxide species in various supported metal oxide catalysts has been probed by different chemical reactions including methanol oxidation, alkane oxidation, SO2 oxidation, and the selective catalytic reduction of NOx. Correlation of the catalytic reactivity with the corresponding molecular structural information about the surface metal oxide species has elucidated many fundamental issues about the catalytic properties of the surface metal oxide species during catalytic reactions, the roles of terminal M=O bonds, bridging M–O–M bonds, adjacent or neighboring sites, secondary metal oxide additives, support ligands, and preparation methods. The fundamental information obtained from these molecular structures-reactivity relationships has great potential for the molecular design of supported metal oxide catalysts for various catalytic applications.

The formation of two-dimensional metal oxide species on surfaces of oxide supports through thermal spreading of three-dimensional bulk metal oxides, schematically represented in Figure 1, is well documented in the catalysis literature. Thermal spreading is a spontaneous process from a thermodynamics perspective. The driving force for thermal spreading and formation of the surface metal oxide species on surfaces of oxide supports through thermal spreading of three-dimensional bulk metal oxides, schematically represented in Figure 1, is well documented in the catalysis literature. Thermal spreading is a spontaneous process from a thermodynamics perspective.
oxide monolayer is a concentration gradient of the dispersed metal oxide or a decrease in the overall system surface free energy. However, its kinetics are constrained because high temperatures are required for surface diffusion or migration of one metal oxide component over the surface of a secondary oxide support to occur at an appreciable rate. In the context of thermal spreading, Tamman temperature \( T_{\text{Tamm}} \approx 0.5 T_{\text{mp}} \), \( T_{\text{mp}} \) = melting point of the bulk metal oxide) is often used to estimate the temperature for thermal treatments.

In contrast, much information is available on the spreading of metal oxides over oxide supports during catalytic reactions. Gasior et al.\(^{(1)}\) previously reported the spreading of V\(_2\)O\(_5\) over the surface of TiO\(_2\) (anatase) grains in their physical mixture occurring at 360 °C during o-xylene oxidation, which was manifested by an increase in both conversion and phthalic anhydride selectivity with reaction time. Cavalli et al.\(^{(12)}\) observed that bulk V\(_2\)O\(_5\) could spread over the TiO\(_2\) (rutile) surface during ammonia oxidation of toluene to benzonitrile at 320–390 °C. The present paper presents direct evidence that reaction-induced spreading of bulk metal oxides onto oxide supports during alcohol oxidation reactions can occur at temperatures significantly below those required for spontaneous thermal spreading of metal oxides.

2. Experimental Section

2.1. Materials. The TiO\(_2\) (P-25, \( \sim 55 \text{ m}^2/\text{g}\)), TiO\(_2\) (anatase), and TiO\(_2\) (rutile) supports were purchased from Degussa. The SnO\(_2\) support (3.7 \text{ m}^2/\text{g}) was obtained from Aldrich. A fumed Cab-O-Sil SiO\(_2\) support (Cabot, EH-5) with a BET surface area of 380 \text{ m}^2/\text{g} was used. For the TiO\(_2\) and SnO\(_2\) supports, treatments with distilled water and subsequent calcination at 550 °C were employed to improve their handling characteristics. MoO\(_3\), V\(_2\)O\(_5\), CrO\(_3\), Cr\(_2\)O\(_7\), Re\(_2\)O\(_7\), WO\(_3\), and Nb\(_2\)O\(_5\) were purchased from Aldrich. Methanol (Alfa, Semiconductor Grade), ethanol (Mc-Cormick, Absolute-200 Proof), and 2-butanol (Aldrich, 99%) were used as reactants for alcohol oxidation. He (Linde, 99.99%), and O\(_2\) (Linde, 99.99%) were procured from Linde.

2.2. Preparation of Binary Metal Oxide Physical Mixtures. Two methods were used to prepare the physical mixtures: (a) combining an appropriate amount of a metal oxide with an oxide support and pentane (Aldrich, 99.5%) in a beaker, vibrating for 15 min in an ultrasonic bath, and drying in air for 16 h at 300 °C; (b) mixing a metal oxide and an oxide support by grinding in an agate mortar for 30 min. No further thermal treatments were performed to these physical mixtures.

2.3. Alcohol Oxidation. Alcohol oxidation over the loose powder physical mixture catalysts was performed in a fixed-bed reactor at atmospheric pressure and in the temperature range of 25–400 °C. The details of the reactor system have been previously described.\(^{(13)}\) A reactant stream of CH\(_3\)OH (or C\(_2\)H\(_5\)OH) and \( 0.2 \text{ atm} \) O\(_2\) was introduced into the reactor at atmospheric pressure and in the temperature range of 25–400 °C. The details of the reactor system have been previously described.\(^{(13)}\)

3. Results

3.1. Thermal Spreading. MoO\(_3\) on TiO\(_2\). The ambient Raman spectra of a 4% MoO\(_3\)/TiO\(_2\) physical mixture, in its loose powder form after a 1-h thermal treatment at temperatures of 400–500 °C in dry air, are shown in Figure 2 in the 700–1100 cm\(^{-1}\) range. After the 400 °C thermal treatment, the Raman spectrum exhibits sharp 990 and 814 cm\(^{-1}\) bands due to crystalline MoO\(_3\), and a broad band at \( \sim 950 \text{ cm}^{-1}\), which was previously assigned to the vibration of a hydrated surface molybdenum oxide species.\(^{(15-17)}\) The ~950 cm\(^{-1}\) Raman band intensity of the

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surface molybdenum oxide species increases with treatment temperatures at the expense of the 990 and 814 cm\(^{-1}\) bands of crystalline MoO\(_3\). After the 1-h thermal treatment at 500 °C, the 990 and 814 cm\(^{-1}\) Raman bands of crystalline MoO\(_3\) almost disappear, and the broad band at 950 cm\(^{-1}\) becomes dominant, indicating that almost complete transformation of bulk MoO\(_3\) into two-dimensional surface molybdenum oxide species occurred. The results are consistent with the previous observation that bulk MoO\(_3\) readily spreads onto the surface of a TiO\(_2\) (P25) support forming a two-dimensional surface metal oxide overlayer when their physical mixtures are thermally treated in dry air at elevated temperatures (400–500 °C).\(^{15-19}\) The high stability of the surface metal oxide overlayer is the consequence of the strong chemical bonding of the surface molybdena species to the TiO\(_2\) surface.

Similar thermal treatments were applied to the self-supporting wafers of the 4 wt % MoO\(_3\)/TiO\(_2\) physical mixture. Interestingly, only a very small amount of the surface molybdenum oxide species formed after the physical mixture pellets were heated at temperatures of 400–500 °C in both dry and wet air, as shown in Figure 3. This result suggests that strong mass transfer limitations exist when the physical mixture is in the form of a self-supporting wafer.

\(\text{V}_2\text{O}_5\) on TiO\(_2\). The Raman spectra of a 4 wt % V\(_2\text{O}_5\)/TiO\(_2\) physical mixture in both loose powder and pellet forms, after 4-h 300–500 °C treatments in dry air, are presented in Figures 4 and 5, respectively. Dehydration of the surface vanadium oxide species was achieved by holding the samples stationary so that the surface vanadium oxide species can be discriminated from the bulk V\(_2\text{O}_5\) crystallites in the Raman spectra. The sharp 990–992 cm\(^{-1}\) Raman band is characteristic of crystalline V\(_2\text{O}_5\) and the weak ~790 cm\(^{-1}\) band is due to the first overtone of the 395 cm\(^{-1}\) band of the TiO\(_2\) (anatase) support. The presence of the weak broad features at ~1022 and/or ~938 cm\(^{-1}\) due to the surface vanadium oxide species reveals that a small amount of crystalline V\(_2\text{O}_5\) had thermally spread onto the TiO\(_2\) support surface when their physical mixture powder samples were treated in dry air at 300–500 °C for 4 h. The ~1022 cm\(^{-1}\) Raman band has been assigned to the V=O vibration of a distorted surface VO\(_4\) species present under dehydrated conditions and the ~938 cm\(^{-1}\) Raman band has been associated with a two-dimensional polymerized VO\(_4\) species.\(^{19}\)

The thermal spreading of V\(_2\text{O}_5\) on TiO\(_2\) reported in the literature is somewhat conflicting regarding the treatment conditions under which the surface vanadium oxide species forms.\(^{16,17,20-22}\) The discrepancies are probably related to the preparation methods of the physical mixtures, their surface areas, and the presence of surface impurities.\(^{23}\)

3.2 Reaction-Induced Spreading. 3.2.1. MoO\(_3\) on TiO\(_2\), SnO\(_2\), and SiO\(_2\), MoO\(_3\) on TiO\(_2\). The ambient Raman spectra of the 4 wt % MoO\(_3\)/TiO\(_2\) physical mixture
samples after 4 h of methanol oxidation at 25 to 230 °C are shown in Figure 6. After methanol oxidation at 25 °C, the Raman spectrum was essentially identical to that of crystalline MoO$_3$ (Figure 6a). Methanol oxidation even at 100 °C, however, leads to the formation of a considerable amount of surface molybdenum oxide species on TiO$_2$, evidenced by the presence of the broad Raman band at $\sim$950 cm$^{-1}$ shown in Figure 6b. It must be noted that the sensitivity for detection of crystalline MoO$_3$ is 17 times more than that for detection of surface molybdenum oxide species.$^{24a}$ Increasing the reaction temperature from 100 to 230 °C leads to the dominance of the surface molybdenum oxide species only with a trace of crystalline MoO$_3$ present in the final catalyst mixture (see Figure 6d). The spreading of bulk MoO$_3$ onto the TiO$_2$ support during methanol oxidation occurred at temperatures that are much lower than the Tammann temperature (261 °C) of crystalline MoO$_3$.

Direct evidence for reaction-induced spreading also comes from the in situ Raman studies during methanol oxidation, as shown in Figure 7 over a catalyst pellet consisting of a 4% MoO$_3$/TiO$_2$ physical mixture at 230 °C. Prior to methanol oxidation, the Raman spectrum only possesses the strong Raman bands of crystalline MoO$_3$ at 814 and $\sim$988 cm$^{-1}$ (see Figure 7a). Upon exposure to the methanol oxidation reaction conditions, the sharp Raman bands due to crystalline MoO$_3$ slowly diminish with reaction time and a new broad Raman band at 969 cm$^{-1}$ is formed (see Figure 7b–e). The in situ Raman band at 969 cm$^{-1}$ has previously been assigned to a surface molybdenum oxide coordinated to a methoxy species.$^{24b}$ When the mixture was switched to an O$_2$/He stream, the Raman band at 969 cm$^{-1}$ shifted toward 990 cm$^{-1}$ due to the decomposition of the surface molybdate methoxy complex to a dehydrated surface molybdenum oxide species (see spectra f and g of Figure 7). Simultaneously, there was also an increase in the crystalline MoO$_3$ 814 and $\sim$988 cm$^{-1}$ Raman bands due to the oxidation of the partially reduced bulk MoO$_3$ particles during the methanol oxidation reaction. Further increase of the reaction temperature to 300 °C for about an hour resulted in the complete disappearance of the crystalline MoO$_3$ Raman bands and only the appearance of the Raman band associated with the surface molybdenum oxide species (not shown here). Further oxidation of the sample at 300 °C again resulted in the appearance of weak crystalline MoO$_3$ Raman bands revealing that some residual reduced MoO$_3$ crystallites still remained and that higher temperature treatment or longer reaction time is required for the complete spreading of bulk MoO$_3$ on the titania support.

The reaction-induced spreading of MoO$_3$ on TiO$_2$ is also reflected by the variation of the methanol oxidation catalytic properties of the physical mixture catalysts with reaction time during methanol oxidation. The dependence of the methanol oxidation activity and formaldehyde selectivity on reaction time was studied over 60 mg of a 4% MoO$_3$/TiO$_2$ physical mixture catalyst at 230 °C and is presented in Figure 8A. The methanol oxidation activity has been normalized to the number of methanol molecules

Figure 5. Raman spectra (obtained by holding the samples stationary) of a 4% V$_2$O$_5$/TiO$_2$ physical mixture in pellet form after 4 h of thermal treatment in dry air at conditions (a) 300, (b) 400, and (c) 500 °C.

Figure 6. Ambient Raman spectra of a 4% MoO$_3$/TiO$_2$ physical mixture in powder form after 4 h of methanol oxidation at reaction temperatures (a) 25, (b) 100, (c) 150, and (d) 230 °C.
The catalytic activity of the physical mixture increases with reaction time from an initial TOF of 0.02 s\(^{-1}\) at 5 min to a final TOF of 0.041 s\(^{-1}\) at 455 min and asymptotically approaches the catalytic activity (TOF) of a 4% MoO\(_3\)/TiO\(_2\) catalyst prepared by alkoxide impregnation (100% dispersed Mo). The selectivity to formaldehyde also increases over the initial 70 min and approaches the formaldehyde selectivity (73%) of the 4% MoO\(_3\)/TiO\(_2\) catalyst prepared by alkoxide impregnation. Previous investigations have revealed that the surface molybdenum oxide species is the active site for methanol oxidation to formaldehyde and that it possesses a much higher TOF than bulk MoO\(_3\). The simultaneous increase in both catalytic activity and formaldehyde selectivity of the 4% MoO\(_3\)/TiO\(_2\) physical mixture catalyst with reaction time directly corresponds to the gradual spreading of bulk MoO\(_3\) onto the TiO\(_2\) support surface. The corresponding Raman spectrum of the 4% MoO\(_3\)/TiO\(_2\) physical mixture catalyst after methanol oxidation (shown in Figure 8B) confirms that almost complete transformation of crystalline MoO\(_3\) into surface molybdenum oxide species has occurred.

The studies were further extended to examine the effects of higher alcohol oxidation (ethanol and 2-butanol) on reaction-induced spreading of MoO\(_3\) on TiO\(_2\). The Raman band intensity ratios \(I_{950}/I_{990}\) of the surface molybdenum oxide species to crystalline MoO\(_3\) in the 4% MoO\(_3\)/TiO\(_2\) physical mixture catalyst after methanol oxidation (shown in Figure 8B) confirms that almost complete transformation of crystalline MoO\(_3\) into surface molybdenum oxide species has occurred. These results demonstrate that the induced spreading of MoO\(_3\) on TiO\(_2\) follows the trend methanol > ethanol > 2-butanol, water. Furthermore, an oxygen-free methanol environment is also highly favorable for the transformation of crystalline MoO\(_3\) into the surface molybdenum oxide species, suggesting that methanol is the key component that is associated with the bulk MoO\(_3\) spreading onto the TiO\(_2\) support surface during methanol oxidation.

The reaction-induced spreading of bulk MoO\(_3\) onto TiO\(_2\) is also reflected in the continuous increase in the higher alcohol (ethanol and 2-butanol) conversion with reaction time as a two-dimensional surface MoO\(_3\) species. These results demonstrate that the induced spreading of MoO\(_3\) on TiO\(_2\) follows the trend methanol > ethanol > 2-butanol, water. Furthermore, an oxygen-free methanol environment is also highly favorable for the transformation of crystalline MoO\(_3\) into the surface molybdenum oxide species, suggesting that methanol is the key component that is associated with the bulk MoO\(_3\) spreading onto the TiO\(_2\) support surface during methanol oxidation.
For comparison, the conversion data for methanol oxidation is also plotted in Figure 10. The methanol conversion over the 4% MoO3/TiO2 physical mixture continuously increased from about 8 to 16% during the first 3 h of reaction. The ethanol and 2-butanol conversions also increased continuously with reaction time but the higher alcohols were more active than methanol due to their weaker R–C–H bonds. Thus, the increase in alcohol conversion as a function of reaction time over the MoO3/TiO2 physical mixture catalysts is directly related to the transformation of crystalline MoO3 into the surface molybdenum oxide species on the TiO2 support.

MoO3 on SnO2. The reaction-induced spreading of bulk MoO3 also readily occurs on different oxide supports during methanol oxidation at mild temperatures. The in situ Raman spectra of a 1 wt % MoO3/SnO2 physical mixture acquired during methanol oxidation and treatments in an O2/He stream at 230 °C are shown in Figure 11. The Raman features at 630 and 775 cm⁻¹ are due to the SnO2 support.25 The sharp 990, 814, and 667 cm⁻¹ Raman bands, characteristic of crystalline MoO3, nearly disappeared after a half hour of methanol oxidation at 230 °C, and a broad band at ~970 cm⁻¹ due to a surface molybdenum oxide methoxy species24b is observed (see Figure 11c). Subsequent reoxidation with O2/He at 230 °C slightly increases the band intensities of both the surface molybdenum oxide species and crystalline MoO3 (see Figure 11d).

MoO3 on SiO2. In the case of MoO3/SiO2 physical mixtures, it is expected that no spreading should be observed during methanol oxidation since the surface molybdenum oxide species are not stable under methanol oxidation reaction conditions.26 The methanol oxidation TOFs of a 4 wt % MoO3/SiO2 physical mixture catalyst as a function of reaction time at 230 °C are shown in Figure 12A. In contrast to the results for the 4 wt % MoO3/TiO2 physical mixture, the methanol oxidation activity of the 4 wt % MoO3/SiO2 physical mixture does not increase with reaction time and does not asymptotically approach the TOF (0.07 s⁻¹) of a 4 wt % MoO3/SiO2 catalyst prepared by alkoxide impregnation (100% dispersed Mo). The formaldehyde selectivity data were not obtained due to the low methanol conversion. Thus, the catalytic results suggest that crystalline MoO3 does not spread onto the SiO2 support during methanol oxidation. The corresponding Raman spectra of the 4 wt % MoO3/SiO2 physical mixture catalyst before and after methanol oxidation (presented in Figure 12B) show that only the Raman bands due to crystalline MoO3 are observed and that the Raman bands due to surface molybdenum oxide species are not present. The Raman bands of crystalline MoO3 after methanol oxidation are much weaker than those before methanol oxidation, suggesting that a significant amount of crystalline MoO3 was lost from the 4 wt % MoO3/SiO2 physical mixture catalyst. This is further confirmed by the observation that a large amount of crystalline MoO3 was found deposited at the cooler exit of the reactor and that the color of the 4 wt % MoO3/SiO2 physical mixture catalyst after methanol oxidation was closer to that of pure SiO2.

3.2.2. V2O5 on TiO2, SnO2, and SiO2. V2O5 on TiO2. The in situ Raman spectra of a self-supported wafer consisting of a 4% V2O5/TiO2 physical mixture during methanol oxidation at 230 °C are shown in Figure 13. The starting sample only exhibits the Raman bands of crystalline V2O5 at about 990 cm⁻¹ and the TiO2 support at about 790 cm⁻¹ (see Figure 13a). Exposure of the 4% V2O5/TiO2 catalyst to the methanol oxidation reaction at 230 °C completely removes the Raman bands of the V2O5...
crystals and no new bands due to surface vanadia species are observed (see Figure 13b-d). The complete absence of any vanadia Raman bands suggests that the vanadia component of the catalyst was reduced since reduced vanadia gives rise to very weak Raman bands.27 Reoxidation of the 4% V2O5/TiO2 physical mixture catalyst wafer resulted in the appearance of a new Raman band at 1022 cm\(^{-1}\) associated with surface vanadia species (see Figure 13e,f)14,17,28 and the complete absence of crystalline V2O5 particles. Thus, the in situ Raman studies demonstrate that crystalline V2O5 completely transformed into the surface vanadium oxide species during methanol oxidation at a very mild temperature, 230 °C.

The structural changes in the V2O5/TiO2 physical mixture catalyst also result in corresponding changes in the methanol oxidation activity and selectivity patterns of this catalyst. The evolution of the activity and formaldehyde selectivity with reaction time is observed during methanol oxidation in a fixed bed reactor with 10 mg of the 4% V2O5/TiO2 physical mixture catalyst wafer. Figure 14A shows the catalytic activity of the V2O5/TiO2 physical mixture catalyst continuously increases with reaction time during the initial methanol oxidation period. When the reaction time exceeded 155 min, corresponding to the time required for complete spreading of V2O5 on TiO2 to occur, a constant activity is observed, which is the same as that (TOF = 0.185 s\(^{-1}\)) of a 4% V2O5/TiO2 catalyst prepared by alkoxide impregnation (100% dispersion of vanadium). The formaldehyde selectivity remained essentially constant at all the conversion levels. The corresponding Raman spectrum of the 4% V2O5/TiO2 physical mixture after methanol oxidation reveals that complete spreading of crystalline V2O5 onto the TiO2 surface as a two-dimensional vanadium oxide species occurred, as shown in Figure 14B. The surface VO\(_x\) species are characterized by the broad Raman bands at 1020 and 930 cm\(^{-1}\).

The influence of different gaseous environments on the spreading of V2O5 on TiO2 is compared in Figure 15. Exposure of the 4 wt% V2O5/TiO2 physical mixture catalyst to the O2/He and H2O/O2/He steams at 230 °C for 4 h resulted in a broad and ill-defined band at about 938 cm\(^{-1}\), in addition to the sharp strong band at 990 cm\(^{-1}\) due to crystalline V2O5 (Figure 15b,c). The Raman band at 990 cm\(^{-1}\) has been assigned to a hydrated polymerized surface vanadium oxide species based on previous Raman and NMR studies.17,29 Upon being exposed to methanol and 2-butanol oxidation conditions at 230 °C for 4 h, the sharp 990 cm\(^{-1}\) band of crystalline V2O5 almost completely disappeared and a broad band of considerable intensity at about 1018 and a weak band at 938 cm\(^{-1}\) were observed for the sample after methanol oxidation (Figure 15d) and only the 938 cm\(^{-1}\) band was present in the sample after 2-butanol oxidation (Figure 15e) since the 1018 cm\(^{-1}\) band is masked by the strong fluorescence. The 1018 cm\(^{-1}\) band is due to dehydrated surface vanadium oxide species, as

![Figure 12](image-url)

**Figure 12.** (A) Plot of methanol oxidation TOF versus reaction time over a 4% MoO3/SiO2 physical mixture catalyst in powder form in comparison with the TOF of a 4% MoO3/SiO2 supported catalyst prepared by impregnation (100% dispersed Mo). (B) Ambient Raman spectra of the 4% MoO3/SiO2 physical mixture catalyst (a) before and (b) after methanol oxidation.

![Figure 13](image-url)

**Figure 13.** In situ Raman spectra of a 4% V2O5/TiO2 physical mixture in pellet form during methanol oxidation: (a) flowing O2/He, room temperature; (b) methanol oxidation, 230 °C, 0.5 h; (c) methanol oxidation, 230 °C, 1 h; (d) methanol oxidation, 230 °C, 3 h; (e) flowing O2/He, 230 °C, 0.5 h; (f) flowing O2/He, 230 °C, 1 h.

a result of laser induced dehydration. Compared to the other samples, the sample exposed to the 2-butanol oxidation conditions possessed strong fluorescence in the 1000 cm$^{-1}$ region. The above results suggest that the efficiency of the reaction-induced spreading for the V$_2$O$_5$/TiO$_2$ physical mixtures follows the trend: methanol, 2-butanol, water, oxygen.

The alcohol conversions over the 4% V$_2$O$_5$/TiO$_2$ physical mixture catalyst during alcohol oxidation are plotted against reaction time and shown in Figure 16. The continuous increase of alcohol oxidation (methanol, ethanol, and 2-butanol) activity with time is consistent with the structural transformation of the 4 wt % V$_2$O$_5$/TiO$_2$ physical mixture catalyst. For methanol oxidation, the methanol conversion continuously increased from about 18 to 37% during the first 115 min of reaction and then exhibited a very sharp increase to 100% at about 140 min. The jump in methanol conversion was accompanied by an increase in the catalyst bed temperature from 230 to 244 °C due to the exothermic heat of reaction.

The reaction-induced spreading of bulk V$_2$O$_5$ can occur on both TiO$_2$ (rutile) and TiO$_2$ (anatase) supports. The Raman spectra (not shown here) of a 1 wt % V$_2$O$_5$/TiO$_2$ (rutile or anatase) physical mixture after 4 h of methanol oxidation at 230 °C exhibit a broad Raman band at about 930 cm$^{-1}$ (see Table 1), characteristic of a polymerized surface vanadium oxide species. The sharp 990 cm$^{-1}$ band of crystalline V$_2$O$_5$ is absent for both samples, demonstrating that crystalline V$_2$O$_5$ has completely spread onto the surfaces of both rutile and anatase TiO$_2$ supports as surface vanadia species.
Experiments were also performed to examine the reaction-induced spreading of bulk V2O5 on SiO2 did not occur either. The methanol oxidation TOSs as a function of reaction time for a 4 wt % V2O5/SiO2 physical mixture catalyst at 230 °C are much lower than the TOF of a 4 wt % V2O5/SiO2 catalyst prepared by impregnation (100% catalyst at 230 °C). The selectivity data were not reported because of the low methanol conversion. The corresponding Raman spectra (not shown here) of the 4% V2O5/SiO2 physical mixture before and after methanol oxidation reveal that crystalline V2O5 has been completely removed from the physical mixture catalyst during methanol oxidation, also evidenced by the fact that the final catalyst exhibits the same color as pure SiO2.

V2O5 on SiO2. Similar to the MoO3/SiO2 system, the reaction-induced spreading of bulk V2O5 on SiO2 did not occur either. The methanol oxidation TOSs as a function of reaction time for a 4 wt % V2O5/SiO2 physical mixture catalyst at 230 °C are much lower than the TOF of a 4 wt % V2O5/SiO2 catalyst prepared by impregnation (100% dispersed V2O5), suggesting that the surface vanadium oxide species do not form on SiO2. The selectivity data were not reported because of the low methanol conversion. The corresponding Raman spectra (not shown here) of the 4% V2O5/SiO2 physical mixture before and after methanol oxidation reveal that crystalline V2O5 has been completely removed from the physical mixture catalyst during methanol oxidation, also evidenced by the fact that the final catalyst exhibits the same color as pure SiO2.

3.2.3. CrO3, Cr2O3, Re2O7, WO3, and Nb2O5 on TiO2. Experiments were also performed to examine the reaction-induced spreading of other metal oxides (CrO3, Cr2O3, Re2O7, WO3, and Nb2O5) on the TiO2 (P-25) support. The results for the 4% MoO3 (M = Cr, Re, W, and Nb)/TiO2 physical mixtures after 2 h of methanol oxidation at 230 and 400 °C are summarized in Table 2 together with above other systems.

The Raman spectrum of a spinning CrO3/TiO2 catalyst pellet exhibits only a band at 790 cm⁻¹ due to the TiO2 support. When the sample was stationary, dehydration induced by the laser beam resulted in a new band at ~1000 cm⁻¹, corresponding to a dehydrated surface chromium oxide species. Under hydrated conditions, this band would shift to ~880 cm⁻¹, which was masked by the high background in this region of the spectrum. Similar to the CrO3/TiO2 catalyst, the Cr2O3/TiO2 catalyst (stationary) also exhibits a weak band at ~1000 cm⁻¹, corresponding to the dehydrated surface chromium oxide species. Interestingly, this result suggests that crystalline Cr2O3 has spread onto the TiO2 surface during methanol oxidation.

The Raman bands of the Re2O7/TiO2 physical mixture after methanol oxidation occurred at ~980 and ~920 cm⁻¹ when the sample was spun. The 980 cm⁻¹ band shifts to ~990 cm⁻¹ due to partial dehydration induced by the laser beam when the sample was held stationary. This behavior is reversible, as demonstrated by the 990 cm⁻¹ Raman band shifting back to 980 cm⁻¹ when the sample is rotated. The current observation is consistent with the previous findings for the Re2O7/Al2O3 catalysts, suggesting that bulk Re2O7 has spread onto the TiO2 surface during methanol oxidation.

The Raman spectra of the 4% Nb2O5/TiO2 physical mixture after 2 h of methanol oxidation at 230 and 400 °C showed that Raman spectra measured by spinning the samples or holding them stationary are almost identical, possessing only the ~790 cm⁻¹ band due to TiO2. Absence of a ~980 cm⁻¹ band due to the dehydrated surface niobium oxide species and a ~890 cm⁻¹ band due to the hydrated surface niobium oxide species indicates that Nb2O5 did not spread onto the surface TiO2 during methanol oxidation.

The Raman spectra of the WO3/TiO2 physical mixture catalyst exhibits very sharp bands at 800 and 713 cm⁻¹, which are characteristic of crystalline WO3 particles. The Raman band due to the surface tungsten oxide species (expected at 1010 cm⁻¹ under dehydrated conditions and ~980 cm⁻¹ under hydrated conditions) is not observed, implying that reaction-induced spreading of WO3 on TiO2 does not occur for this system under these mild reaction conditions.

4. Discussion

4.1. Thermal Spreading. It is well-known that surface diffusion or migration has played an important role in formation of heterogeneous catalysts. Thermal spreading is believed to be related to surface migration or diffusion of one component over the surfaces of an oxide support and high temperature is required to overcome the intrinsic resistance coming from the generally high lattice energies of active components. As a rule, thermal treatment temperatures must be higher than the Tammann temperature of the metal oxide in order for surface diffusion to occur at an appreciable rate. When the 4%MnO3/TiO2 physical mixture is heated at 400–500 °C, it is not surprising that a significant amount of crystalline MnO3 has transformed into surface molybdenum oxide species (see Figure 2) because the heating temperatures are much higher than the Tammann temperature of MnO3 (T_Tammann = 261 °C). The higher the heating temperature, the more the crystalline MnO3 transforms into the surface molybdenum oxide species due to higher surface diffusion or migration rate at higher temperatures. In contrast to prediction, only a small amount of V2O5 spread onto TiO2 after their physical mixture was heated at 300–500 °C for 4 h in dry air (see Figures 4 and 5) even though the heating temperatures were also much higher than the Tammann temperature of crystalline V2O5 (206 °C). Conflicting results were reported in the literature regarding thermal dispersion of the V2O5/TiO2 system. Haber et al. and Honig et al. did observe significant spreading of V2O5 on TiO2 after thermal treatment in dry air at 450 °C for 1 h or 500 °C for 48 h for their physical mixtures made by grinding in an agate mortar. In contrast, Leyrer et al. showed that thermal spreading of V2O5 on TiO2 did not occur after a hand-grinding physical mixture was thermally treated at 500 °C for 4 h in dry O2. Hausinger et al. demonstrated that the spreading tendency of V2O5 on TiO2 was influenced by mixing methods of their physical mixtures.

4.2. Reaction-Induced Spreading. 4.2.1. Factors Influencing Reaction-Induced Spreading. Effect of Temperature. The temperature range at which metal
oxides spread over oxide supports allows for the discrimination between reaction-induced spreading and thermal spreading. Thermal spreading of crystalline MoO₃ on TiO₂ requires a temperature of at least 300–350 °C since its Tammann temperature is 261 °C.¹⁷ During methanol oxidation, crystalline MoO₃ spreads onto the TiO₂ surface as a surface molybdenum oxide species at a temperature even as low as 100 °C (see Figure 6). The possibility of any hot spots in the fixed-bed reactor can be ruled out because the methanol conversion is negligible at 100 °C and ~5% at 150 °C, and thus, the exothermic heat of reaction is negligible. Thus, reaction-induced spreading of metal oxides during methanol oxidation generally occurs at much lower temperatures than the Tammann temperature of crystalline MoO₃, which indicates that thermal-induced spreading does not account for this phase transformation and that a strong interaction between the gas-phase components and crystalline MoO₃ must be occurring. Increasing the methanol oxidation reaction temperature from 100 °C to 230 °C leads to a significant increase in the extent of spreading (see Figure 6).

The bulk metal oxides (MoO₃, V₂O₅, and Cr₂O₃) do not thermally spread onto oxide supports at 230 °C because of their higher Tammann temperatures (listed in Table 1). Therefore, spreading of these metal oxides on the oxide supports (TiO₂ and SnO₂) during methanol (methanol, ethanol, and 2-butanol) oxidation must correspond to the mechanism of reaction-induced spreading. For Cr₂O₃ and Re₂O₇, thermal-induced spreading is probably also occurring during methanol oxidation at 230 °C due to their relatively low Tammann temperatures (~38 and 12 °C, respectively).

The reaction-induced spreading of bulk MoO₃ and V₂O₅ on TiO₂ and SnO₂ also readily occurs in the pellet catalysts during methanol oxidation at 230 °C (see Figures 7, 11, 13, and Table 2), despite mass transfer limitations in the pellets because of the rapid spreading of bulk MoO₃ and V₂O₅ during methanol oxidation.

**Effect of the Gaseous Components.** Several research groups found that the presence of water vapor influences the spreading rate of bulk MoO₃,¹⁶,⁴⁰ V₂O₅,¹⁶,⁴⁰ and V₂O₅,¹⁶,⁴³ onto various oxide supports, but moisture is not essential for thermal spreading. These authors suggested that volatile metal oxyhydroxide intermediates such as MoO₂-

**Table 1. Surface Free Energies, Melting Points, and Tammann Temperatures of Metal Oxides and Oxide Supports**

<table>
<thead>
<tr>
<th>oxide</th>
<th>γ/10⁻⁶ J cm⁻²</th>
<th>T_max/°C</th>
<th>T_tamb/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO₂</td>
<td>197</td>
<td>38</td>
<td>261</td>
</tr>
<tr>
<td>Re₂O₇</td>
<td>3–4</td>
<td>12</td>
<td>261</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>297</td>
<td>12</td>
<td>261</td>
</tr>
<tr>
<td>MoO₃</td>
<td>8–9</td>
<td>209</td>
<td>600</td>
</tr>
<tr>
<td>WO₃</td>
<td>5–7</td>
<td>795</td>
<td>261</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>10</td>
<td>1474</td>
<td>600</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1512</td>
<td>620</td>
<td>1081</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2454</td>
<td>813</td>
<td>1221</td>
</tr>
<tr>
<td>SnO₂</td>
<td>90</td>
<td>1713</td>
<td>720</td>
</tr>
<tr>
<td>SiO₂</td>
<td>68–70</td>
<td>2054</td>
<td>890</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>110–115</td>
<td>2800</td>
<td>1263</td>
</tr>
<tr>
<td>MgO</td>
<td>90</td>
<td>1975</td>
<td>851</td>
</tr>
<tr>
<td>ZnO</td>
<td>59–80</td>
<td>2715</td>
<td>1221</td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


is more stable than the ethoxy complex, and the ethoxy complex is more stable than the 2-butoxy complex. Consequently, the greater volatility and stability of M-methoxy complexes are responsible for the faster reaction-induced spreading kinetics observed during methanol oxidation.

**Effect of Oxide Supports.** The current studies reveal that reaction-induced spreading of bulk MoO₃ and V₂O₅ readily occurs on TiO₂ and SnO₂ supports, but is not observed for the SiO₂ support. The previous work on thermal spreading also claimed that surface metal oxide species could not be readily achieved on the SiO₂ support and, thus, conflicting results have been reported in the catalysis literature.⁷⁻⁸,¹⁶,²²,⁵⁰ Several research groups demonstrated that salts and metal oxides (especially bulk MoO₃) could spread onto SiO₂ when their physical mixtures were heated.⁸,⁹ However, other authors excluded the possibility of thermal spreading of bulk metal oxides on SiO₂.⁸ Consequently, alternate preparation methods such as impregnation and gas-phase grafting have been widely used to achieve higher dispersions of metal oxides onto the SiO₂ surface. Furthermore, the surface metal oxide species on SiO₂ is not thermally stable because physical mixtures of SiO₂-supported metal oxides with other oxide supports result in complete migration of the surface metal oxide species from SiO₂ to the other oxide supports (e.g., TiO₂) upon thermal treatment.⁵¹ The difficulty of wetting the SiO₂ surface by other metal oxides is related to the low interaction energy between the metal oxides and SiO₂ due to the hydrophobic character, low surface OH density, and reactivity of the SiO₂ surface.¹⁰

The stability of the surface metal oxide species on SiO₂ in the presence of water and alcohol vapors is extremely low and is reflected by the observation that water and methanol can transform the surface metal oxide species to crystalline bulk metal oxides through the formation of mobile and volatile metal oxide species.¹²,²⁶,⁵² During methanol oxidation over silica-supported catalysts, the transformation of surface metal oxide species to their corresponding bulk metal oxides is dominant, and its reverse process of reaction-induced spreading is essentially absent. Therefore, there is a good correlation between reaction-induced spreading and the stability of surface metal oxide species on a specific support in the presence of alcohols. This relationship allows us to classify the oxide supports in two groups: group I consists of only SiO₂ on which the surface metal oxide species is not stable in the presence of alcohols and reaction-induced spreading does not occur during alcohol oxidation reactions, and group II consists of TiO₂, SnO₂, Al₂O₃, ZrO₂, and CeO₂ that favor and stabilize the surface metal oxide species in the presence of alcohols and reaction-induced spreading readily occurs during alcohol oxidation reactions.

The specific TiO₂ phase (anatase and rutile) does not influence the reaction-induced spreading kinetics of bulk V₂O₅ because the same surface vanadium oxide species is present on both anatase and rutile TiO₂ supports after methanol oxidation (see Table 2). Previous structure-reactivity studies also reveal that the TiO₂ phases (anatase, rutile, brookite, and B) do not influence the molecular structure and reactivity of the surface vanadium oxide species.⁵³

**Effect of Bulk Metal Oxides.** Metal oxides with lower melting points and Tammann temperatures (e.g., CrO₃, MoO₃, V₂O₅, and Re₂O₇) can readily spread onto TiO₂ as the surface metal oxide species during methanol oxidation at 230 °C. In contrast, metal oxides with higher melting points and Tammann temperatures (e.g., WO₃ and Nb₂O₅) do not readily transform into the surface metal oxide species on TiO₂ during methanol oxidation reactions at the same temperature (see Table 2). The metal oxides with higher melting points imply a higher stability of the crystalline structures due to their high cohesive or lattice energies. Transformation from a crystalline state into an amorphous surface metal oxide species requires a much stronger interaction between the metal oxides and the gaseous components than the interaction among the crystalline lattices, which were not fulfilled in current methanol reaction conditions.

The oxidation state of the cations in the bulk metal oxides is not as important in reaction-induced spreading as in thermal spreading since thermal spreading is significantly retarded for reduced metal oxide phases that usually possess very high Tammann temperatures.⁹,³⁸ However, essentially complete dispersion of bulk V₂O₅ on TiO₂ was observed during methanol oxidation even though the in situ Raman spectra revealed that the vanadia was reduced under the reaction conditions (see Figure 13). Essentially complete dispersion of bulk MoO₃ on TiO₂ was also observed after treatment of the catalyst in an oxygen-free methanol environment (see Figure 9). Furthermore, reaction-induced spreading of bulk Cr₂O₃, a reduced bulk metal oxide, on TiO₂ was observed to occur during methanol oxidation even at 230 °C (see Table 2). In view of the extremely high Tammann temperature of Cr₂O₃ (1081 °C), thermal spreading should be infeasible at such a mild temperature. The literature previously suggested

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that CrO₂ (T_{Tam} = -36 °C) and CrO₂ (T_{Tam} = -38 °C) might be the mobile phase assisting the spreading process of Cr₂O₃ under certain circumstances. Thus, reaction-induced spreading of Cr₂O₃ during methanol oxidation might be assisted by trace amounts of surface Cr₂O₃ and/or CrO₂ that have low Tammann temperatures through the formation of Cr—methoxo complexes. Therefore, the oxidation states of the metal oxides do not significantly influence the kinetics of reaction-induced spreading of crystalline metal oxides and reaction-induced spreading must proceed by mechanisms different from thermal spreading.

4.2.2. Driving Force and Mechanisms of Reaction-Induced Spreading. Similar to thermal spreading, reaction-induced spreading is a solid-state wetting (solid/solid adsorption) phenomenon, and thus, the driving force for reaction-induced spreading is also a decrease in the overall surface free energy or a concentration gradient of the dispersed metal oxide. However, the kinetics of reaction-induced spreading are modified by interaction (or reaction) of alcohol with spreading metal oxides.

As discussed above, alcohols (methanol, ethanol, and 2-butanol) possess the functional C—OH groups that are responsible for the efficient transformation of bulk crystalline metal oxides into the two-dimensional surface metal oxide species on oxide supports via the formation of M—alkoxy complexes. Reaction-induced spreading of a bulk metal oxide onto an oxide support surfaces assisted by alcohol involve the following steps: (a) attack of the crystalline metal oxide by alcohol molecules to form M—alkoxy complexes, (b) transfer of the M—alkoxy complexes from the crystalline metal oxide to the oxide-support surfaces, and (c) transformation of the M—alkoxy complexes into surface metal oxide species to stabilize on the oxide support surfaces.

Step b can be considered in the following two ways: (i) transport by surface diffusion or migration in a concentration gradient of the surface M—alkoxy complexes; (ii) gas-phase volatilization/readsoption of the volatile M—alkoxy complexes. It is well-known that metal—alkoxy species are the reaction intermediates of alcohol oxidation over supported metal oxide catalysts. The mobility of the surface M—alkoxy complexes is directly related to the number of alkoxyl groups attached to the metal cation. The greater the number of alkoxyl groups, the more mobile the surface M—alkoxy complexes will be. Even volatile M—alkoxy compounds could form under alcohol oxidation conditions, as evident from the observation that bulk MoO₃ and V₂O₅ can be transported from the reactor to the cooler exit of the reactor during methanol oxidation. In the case of physical mixture, the oxide supports can trap the gas-phase M—alkoxy compounds to react with their surface hydroxyls, resulting in formation of surface M—alkoxy complexes. The dramatic temperature difference between reaction-induced spreading and thermal-induced spreading is directly related to the mobile M—alkoxy complexes formed during alcohol oxidation.

The mechanism of reaction-induced spreading corresponds to a mechanism previously proposed for thermal spreading. The authors assumed thermal spreading to contain two steps: (a) a “molecule” leaves its metal oxide surface for the external surface of a support and (b) the “molecule” further diffuses on the support surface. It was found that for solid compounds with high melting points step a is the rate-determining step and that for compounds with low melting points step b is the rate-determining step. The presence of alcohols can greatly facilitate the first step as well as the second step by formation of mobile metal—alkoxy complexes or volatile alkoxide as transporting intermediates, and thus, the activation energy and temperature required for spreading are dramatically decreased with assistance of alcohols.

4.2.3. Catalytic Properties. It has been well documented that the surface metal oxide species of the supported metal oxide catalysts are the active sites, which control the catalytic properties. The current studies clearly demonstrate that the methanol oxidation activity and the formaldehyde selectivity of the binary oxide physical mixture catalysts asymptotically approach the catalytic properties of their corresponding supported metal oxide catalysts prepared by impregnation (100% dispersion) (see Figures 8A and 14A). The changes in the catalytic properties as a function of reaction time correspond to the transformation of the active components from three-dimensional metal oxides into two-dimensional surface metal oxide species on the oxide supports. The final methanol TOF and formaldehyde selectivity of the 4% V₂O₅/TiO₂ physical mixture catalyst are essentially the same as those of the 4% V₂O₅/TiO₂ supported catalyst prepared by impregnation, suggesting that essentially all of the crystalline metal oxides spread onto the TiO₂ surface as surface vanadium oxide species. The Raman spectrum of the final catalyst confirms the complete spreading of crystalline V₂O₅ (see Figure 14A). However, changes in catalytic properties with reaction time were not observed for the physical mixture catalysts comprised of bulk metal oxides and the SiO₂ support because the surface metal oxide species did not form on the SiO₂ surface during methanol oxidation (see Figure 12 and Table 2). The data in Figures 10 and 16 also reveal that the conversions of ethanol and 2-butanol oxidation reactions over the physical mixture catalysts increase with reaction time, implying the occurrence of an analogous transformation from three-dimensional metal oxides into the active surface metal oxide species during the alcohol oxidation reactions.

In the catalysis literature, synergetic effects involving oxygen spillover of active species in selective oxidations over mixed metal oxide catalysts have been proposed to play a determining role in catalysis. This phenomenon might be related to reaction-induced spreading, where one metal oxide migrates or “spills over” to the surface of another metal oxide. The possibility that reaction-induced spreading occurs during selective oxidation reactions over physical mixture catalysts needs to be carefully examined and eliminated before other mechanisms are proposed to explain the observed synergetic effects of physical mixture catalysts.

4.2.4. Implications for Catalyst Preparation. A very important consequence of reaction-induced spreading of bulk 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 oxidation reactions (especially methanol oxidation). The current findings that reaction-induced spreading of bulk metal oxides on oxide supports can occur during oxidation reactions, especially methanol oxidation, at very low temperatures also have important implications for commercial applications. They provide an alternate and unique route for the preparation of supported metal oxide catalysts.
5. Conclusions

A new phenomenon of reaction-induced spreading of bulk metal oxides on oxide supports as a two-dimensional metal oxide overlayer was observed during alcohol oxidation at temperatures much lower than that required for thermal spreading. The reaction-induced spreading proceeds through formation, surface diffusion and volatilization/readsorption of metal–alkoxy complexes. Many factors (e.g., catalyst temperature, gaseous component, oxide support, and metal oxide) were found to influence the transformation kinetics of three-dimensional crystalline metal oxides into two-dimensional surface metal oxide species. Increasing the reaction temperature increases the spreading rate. The gaseous components assist the metal oxide spreading in the following order: methanol ≫ ethanol > 2-butanol, water ≫ oxygen, helium. The high effectiveness of methanol-assisted spreading corresponds to the high volatility and stability of the metal–methoxy complexes. There are two categories of oxide supports: (1) SiO₂, on which the reaction-induced spreading does not occur and the reverse process of transformation of surface metal oxide species to crystallites dominates; (2) oxide supports (e.g., TiO₂ and SnO₂), where reaction-induced spreading of bulk metal oxides (e.g., CrO₃, Cr₂O₃, MoO₃, V₂O₅, and Re₂O₇) readily occurs during alcohol oxidation at mild temperatures. Bulk WO₃ and Nb₂O₅ do not readily transform into surface metal oxide species during alcohol oxidation due to their high cohesive and lattice energies. The oxidation states of the spreading metal oxides do not appear to influence the kinetics of reaction-induced spreading. The alcohol oxidation catalytic properties were found to correspond to the transformation of crystalline metal oxides into the surface metal oxide species, which are the active sites for alcohol oxidation. Both methanol oxidation activity and formaldehyde selectivity of the physical mixture catalysts can reach those of their corresponding supported metal oxide catalysts after sufficient exposure to the reaction environment. Supported metal oxide catalysts can be made using reaction-induced spreading as an alternate and unique route to avoid handling large amounts of salt solutions during coprecipitation and the use of expensive precursors in alkoxide impregnation.

Acknowledgment. Financial support of the Division of Basic Energy Sciences of the Department of Energy, grant DEFG02-93ER14550, is gratefully acknowledged. LA9807210