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Molecular design of supported metal oxide catalysts: an initial step to theoretical models

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Abstract

Molecular design of supported metal oxide catalysts is now possible from molecular level information obtained from Raman spectroscopy and the methanol oxidation reaction. The important factors that influence the molecular design of the supported metal oxide catalysts are the specific oxide support and the specific surface metal oxide. The structure or modification of the oxide support, however, has no effects on the surface metal oxide structure and reactivity. The surface coverage of the specific surface metal oxide, however, influences the reactivity during the methanol oxidation reaction. The synthesis method is not critical since it does not influence the surface metal oxide structure or reactivity. Calcination temperature is not important as long as moderate temperatures (350–500°C) are used. The current fundamental information available about the physical and chemical characteristics of the supported metal oxide catalysts provides a foundation for theoretical models to be developed with respect to their solid–solid and solid–gas interactions.

Key words: methanol oxidation; Raman spectroscopy; reactivity; structure; supported metal oxides

Introduction

Two-dimensional transition metal oxide overlayers are formed when one metal oxide component (*i.e.*, Re_2O_7 , CrO_3 , MoO_3 , WO_3 , V_2O_5 , Nb_2O_5 , *etc.*) is deposited on a second metal oxide substrate (*i.e.*, Al_2O_3 , TiO_2 , SiO_2 , *etc.*) [1–4]. The molecular structures and reactivity of these surface metal oxide species have been intensively investigated over the past decade because of the importance of these supported metal oxide materials in numerous catalytic applications [1–5]. Most of the structural information about these surface metal oxide species has been derived from Raman spectroscopy studies because of its ability to discriminate between different metal oxide species that may simultaneously be present in the catalyst. The reactivity studies have demonstrated that these surface metal oxide species are the active sites for many catalytic

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reactions. The combined structural and reactivity information currently available about these oxide catalysts is making it possible to molecularly design supported metal oxide catalysts based on experimentally derived models.

The molecular design of supported metal oxide catalysts requires that we specify the synthesis method, oxide support, catalyst composition, calcination temperature, location and structure of the surface metal oxide species, as well as its reactivity. Consequently, the influence of each of the above parameters upon the catalytic properties of supported metal oxide catalysts needs to be examined. The present study primarily focuses on the molecular design aspects of supported vanadium oxide catalysts because these catalysts constitute a very important class of heterogeneous oxide catalysts [6]. Comparison with other supported metal oxide systems (MoO_3 , Re_2O_7 , and CrO_3) will also be made to provide a broader perspective. The models derived based on experimental observations can be used to develop theoretical models to gain further insight into the various solid–solid and solid–gas interactions involving the surface metal oxide species.

Experimental

A number of oxide supports were employed in the present study. Some of the specifications of these oxide supports are presented in Table 1. Many dif-

TABLE 1

Support specifications

Oxide support	Surface area (m^2/g)
Al_2O_3 (Harshaw)	180
SiO_2 (Cabot)	300/380
ZrO_2 (Degussa)	39
Nb_2O_5 (Niobium Products Co.)	55
TiO_2 (Degussa, P-25)	55
TiO_2 (anatase) (Laboratory prepared, A22)	22
TiO_2 (rutile) (Laboratory prepared, R28)	28
TiO_2 (anatase + brookite) (Laboratory prepared, BT110)	110
TiO_2 (B phase) (Laboratory prepared, B18)	18

ferent synthesis methods were used to prepare the supported metal oxide catalysts. In the case of supported vanadium oxide catalysts, the catalysts were prepared by vapor phase grafting with VOCl_3 , non-aqueous impregnation (vanadium alkoxides), aqueous impregnation (vanadium oxalate and ammonium metavanadate), as well as dry impregnation with crystalline V_2O_5 (spontaneous dispersion). Supported chromium oxide, rhenium oxide and molybdenum oxide catalysts were prepared by the incipient-wetness impregnation method using an aqueous solution of chromium nitrate, HReO_4 , and ammonium heptamolybdate, respectively.

The molecular structures of the supported metal oxide catalysts were characterized by laser Raman spectroscopy under *in situ*, dehydrated, and ambient conditions. The laser Raman spectroscopy consist of a Spectra Physics Ar^+ laser producing 1–100 mW of power measured at the sample. The scattered radiation was focussed into a Spex Triplemate spectrometer coupled to a Princeton Applied Research OMA III optical multichannel analyzer. About 100–200 mg of the pure catalysts were made into wafers and used for obtaining the Raman spectra in the *in situ* mode. For ambient Raman spectra 5–20 mg of catalysts was placed on a KBr backing. Pure catalyst wafers were also used to obtain ambient Raman spectra.

The supported metal oxide catalysts were examined for their reactivity in the methanol oxidation reaction. The reactor was operated in the differential mode by controlling the amount of catalyst so as to keep conversions below 20%. A methanol/oxygen/helium mixture of ca. 6/13/81 (molar fraction) at 1 atm pressure was used as the reactant gas for all the data presented. The analysis was performed on an online gas chromatograph (GC) (HP 5840A) containing two columns (Poropak R and Carbosieve SII) and two detectors (FID and TCD). Reaction data at 230 °C are presented in the form of turnover number (TON) – defined as the number of moles of methanol converted per mole of vanadium atom per second. The reaction data for some catalysts were also obtained at 200, 230, 240 °C to calculate the activation energy. Calculations involving the determination of heat and mass transfer limitations indicate that no heat or mass transfer limitations exist.

Results and discussion

It is well known that supported metal oxide catalysts possess surface metal oxide phases that are formed by the reaction of the deposited metal oxides with the surface hydroxyls of the high surface area oxide supports. Direct evidence for the titration of the support surface hydroxyls by the deposited metal oxides is obtained from *in situ* infrared (IR) studies and by monitoring the chemisorption of CO_2 [7–9]. Consequently, a necessary condition for the formation of surface metal oxide overlayers is the presence of reactive surface hydroxyls on the oxide support. Oxide supports such as Al_2O_3 , TiO_2 , ZrO_2 , and Nb_2O_5

have a high surface density of reactive surface hydroxyls and tend to form a close-packed monolayer of the surface metal oxide phase, whereas, oxide supports such as SiO_2 which have a lower density of reactive surface hydroxyls and do not form a close-packed overlayer of the surface metal oxide phase. The maximum concentration of the surface metal oxide species (metal atoms/ nm^2) obtained on the different oxide supports (monolayer coverages), determined by Raman spectroscopy which readily discriminates between the two-dimensional overlayer and crystallites, is presented in Table 2. The data presented in Table 2 show that for a specific supported metal oxide phase the surface concentration is similar on all the supports with the exception of SiO_2 . For the SiO_2 support, the monolayer metal oxide concentrations is always about an order of magnitude lower than on the other oxide supports. Recent studies employing electrochemical methods [10] and non-aqueous allyl preparation [11] have demonstrated that somewhat higher surface concentration on SiO_2 can be achieved with these special preparations, but still resulted in only a fraction of the maximum surface concentration that can be achieved on other oxide supports. Furthermore, comparison of the different surface concentrations at monolayer coverages of surface metal oxides indicate almost twice the amount of vanadium oxide present on the surface compared to molybdenum oxide and rhenium oxide. The surface concentration at monolayer coverages of chromium oxide on TiO_2 and ZrO_2 are difficult to determine due to the overlap of the support signals. Despite this irregular behavior for supported vanadium oxide it is evident that the surface hydroxyl chemistry controls the formation, location, and maximum concentration of the surface metal oxide species present in supported metal oxide catalysts.

The molecular structures of the surface metal oxide species present in the metal oxide overlayer are not well understood and the influence of surface coverage (catalyst composition), specific oxide support, preparation method, and calcination temperature need to be established. To determine the effect of

TABLE 2

Surface metal oxide concentration of different oxide supports at monolayer loadings

Oxide support	Surface area (m^2/g)	Surface concentration (metal atoms/ nm^2)			
		V_2O_5	MoO_3	CrO_3	Re_2O_7
Al_2O_3	180	6.8	3.4	3.7	2.3
TiO_2	55	6.8	4.3	6.2 ^a	2.6
ZrO_2	39	6.4	3.2	7.4 ^a	3.8
Nb_2O_5	55	6.8	3.6	4.0	^b
SiO_2	300	0.6	0.4	0.6	0.6

^aMonolayer loadings difficult to determine due to overlap of support peaks.

^bNot determined.

oxide support on the structure and reactivity of the surface metal oxide phase, a series of low coverage (ca. 1 wt.%) supported metal oxide catalysts were prepared. The low loading catalysts were selected because at these surface coverages potential complication due to additional surface metal oxide species could be eliminated [12-15]. The *in situ* Raman spectra of the low loadings of metal oxide are shown in Figs. 1 to 4. The surface vanadium oxide species on the different oxide supports exhibit a Raman band at 1015-1040 cm^{-1} due to the terminal V=O bond of isolated VO_4 species [12,13,15]. The surface molybdenum oxide species on the different supports possess a Raman band at 978-1006 cm^{-1} due to terminal Mo=O bond of isolated MoO_5 species [10,13]. The surface chromium oxide species on the different oxide supports show Raman bands at 986-1010 cm^{-1} and 850-875 cm^{-1} . The Raman band at ca. 1000 cm^{-1} is due to the terminal Cr=O band of isolated CrO_4 species and the band at ca. 865 cm^{-1} is characteristic of polymerized CrO_4 species [16]. The surface rhenium oxide species on the different supports possesses Raman bands at 990-1005 cm^{-1} and 878-884 cm^{-1} . The Raman band at ca. 1000 cm^{-1} is due to the terminal Re=O bond of isolated ReO_4 species and the band at ca. 880 cm^{-1} is the associated asymmetric stretch [14]. The strong band at 795 cm^{-1} for the 1% $\text{Re}_2\text{O}_7/\text{TiO}_2$ originates from the TiO_2 support. The *in situ* Raman bands for each specific surface metal-oxygen system, in Figs. 1 to 4, are essentially the same on the different oxide supports. The similarity of the metal-oxygen vibrations of the surface metal oxide species suggests that essentially the same surface metal oxide species is present on the different oxide supports at these

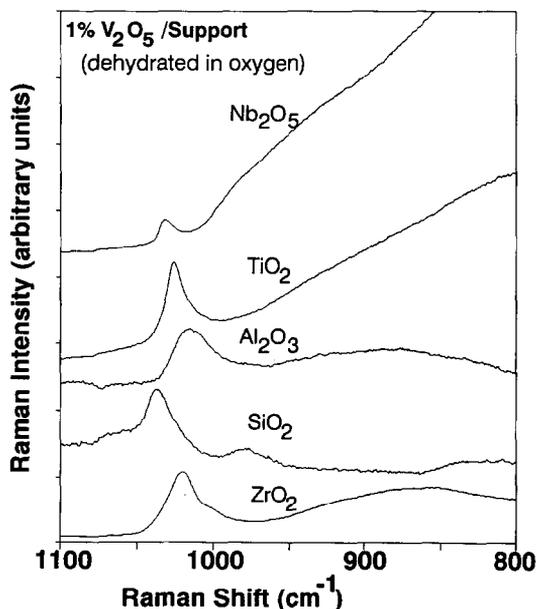


Fig. 1. Dehydrated Raman spectra of 1% V_2O_5 on different oxide supports.

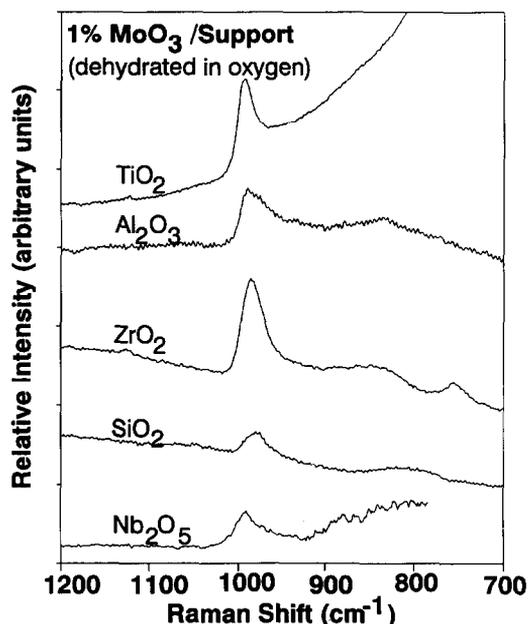


Fig. 2. Dehydrated Raman spectra of 1% MoO₃ on different oxide supports.

metal oxide loadings. This conclusion is also supported by other characterization studies such as solid state vanadium-51 NMR studies [5]. Thus, the dehydrated surface metal oxide molecular structures at low loadings are independent of the specific oxide support.

The reactivity of the surface metal oxide species on the different oxide supports was probed by the methanol oxidation reaction. The methanol oxidation reaction is very sensitive to the nature of the surface sites present in oxide catalysts. Surface redox sites (sites that are capable of being reduced and oxidized) form primarily formaldehyde and to a lesser extent methyl formate and dimethoxy methane (at low conversions) as the reaction products. Surface acid sites result in the formation of dimethyl ether. For the case of supported vanadium oxide catalysts, the surface vanadia redox sites produced formaldehyde almost exclusively, with the exception of V₂O₅/Al₂O₃. For the V₂O₅/Al₂O₃ system, only a trace of formaldehyde was formed because the surface Lewis acid sites of the alumina support formed dimethyl ether. Thus, for the V₂O₅/Al₂O₃ system the formaldehyde produced was taken as representative of the reactivity of the surface vanadia redox sites. The reactivity, in terms of TON, of the surface vanadia species on different oxide supports was found to dramatically depend on the specific oxide support and decrease in the following order: V₂O₅/ZrO₂ ($3.3 \times 10^0 \text{ s}^{-1}$) ca. V₂O₅/TiO₂ ($2.0 \times 10^0 \text{ s}^{-1}$) > V₂O₅/Nb₂O₅ ($8 \times 10^{-1} \text{ s}^{-1}$) \gg V₂O₅/Al₂O₃ ($3.6 \times 10^{-2} \text{ s}^{-1}$) > V₂O₅/SiO₂ ($3.9 \times 10^{-3} \text{ s}^{-1}$). Similar trends in reactivity as a function of oxide support are also observed for supported molybdenum oxide, rhenium oxide, and chromium oxide. Hence, the

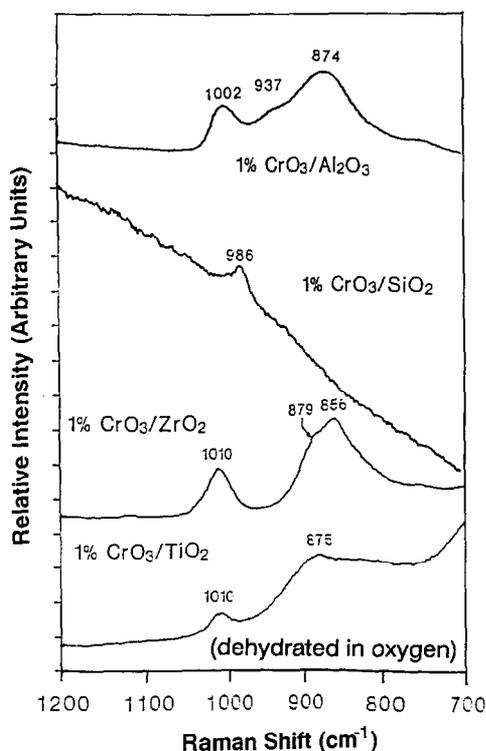


Fig. 3. Dehydrated Raman spectra of 1% CrO₃ on different oxide supports.

specific oxide support is a critical parameter since it has such a profound effect on the reactivity of the surface metal oxide species.

The origin of this support effect in redox reactions, however, is not fully understood in the literature. With the structural information derived above, the difference in reactivity is not a structural factor since the structure is independent of the oxide support. One of the possible factors controlling the reactivity of various supported metal oxide catalysts as a function of oxide support is the difference in the terminal M=O bond or the bridging M-O-support bond. A plot of TON *versus* Raman M=O position for supported vanadium oxide, molybdenum oxide, rhenium oxide, and chromium oxide catalysts suggests that no relationship exists between the catalyst reactivity and the terminal M=O bond strength as shown in Fig. 5. A more plausible conclusion is that the reactivity is related to the bridging M-O-support bond since the surface metal oxide species are generally very reactive when deposited on TiO₂ and ZrO₂ and generally exhibit low reactivity when deposited on Al₂O₃ and SiO₂ [12]. The importance of the M-O-support bond suggests that the reactivity should also be a function of the specific metal oxide species. Indeed, supported molybdenum oxide and chromium oxide catalysts are generally about

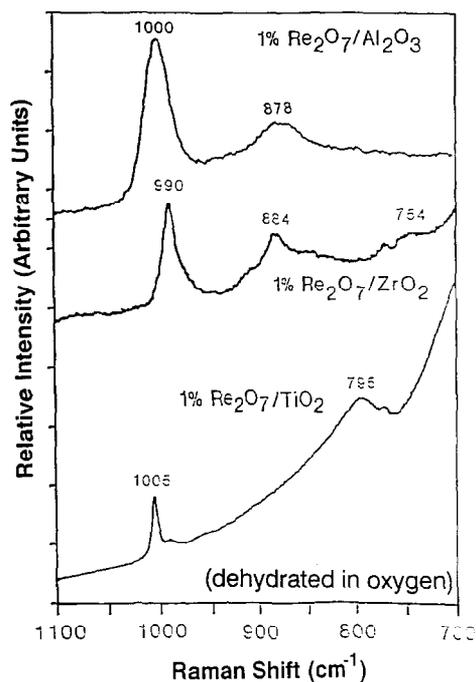


Fig. 4. Dehydrated Raman spectra of 1% Re_2O_7 on different oxide supports.

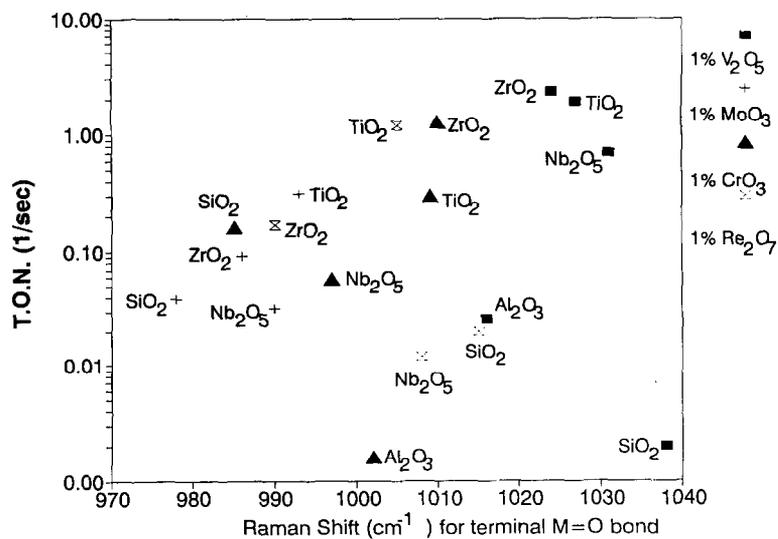


Fig. 5. The methanol oxidation TON of supported metal oxide catalysts as a function of the terminal $\text{M}=\text{O}$ bond (Raman) frequency.

one order of magnitude less reactive than supported vanadia and rhenia catalysts confirming the importance of the M–O-support bond in redox reactions.

Additional information about the reactivity was obtained by determining the kinetic parameters involved during the methanol oxidation reaction for vanadia, molybdena, rhenia, and chromia supported on the different oxide supports. For all these systems the activation energy is approximately the same, 18–22 kcal/mol. The activation energy corresponds to that expected for the breaking of the C–H bond of a surface methoxide intermediate [17,18], $\text{CH}_3\text{O}_{\text{ads}}$, and should be independent of the specific catalyst. The independence of the activation energy with respect to oxide support and supported metal oxide phase implies that the pre-exponential factors vary by orders of magnitude as the oxide support is changed.

The pre-exponential factors depend on the number of active sites or the activity per site, and the differences in pre-exponential factors suggest that either or both of these factors are responsible for these differences. For example, in calculating the TON we assume that all the surface metal oxide species are participating in the reaction all the time. However, the different pre-exponential factors may be due to the fact that on less reducible oxide supports such as Al_2O_3 and SiO_2 only a small fraction of the surface metal oxide species participate at a given time in the reaction, and that for reducible oxide supports such as TiO_2 , ZrO_2 , and Nb_2O_5 a significantly larger fraction of the surface metal oxide species participate at a given time in the reaction. In addition, the different pre-exponential factors may also be due to the difference in the activity per active site. Experiments are currently in progress to discriminate among these various possibilities. Thus, the oxide supports control the reactivity of the surface metal oxide species during redox reactions by controlling the number of active metal oxide sites and/or the activity per metal oxide site.

To study the effect of catalyst composition (metal oxide surface coverage), various loadings of vanadium oxide were deposited on titania (Degussa, $55 \text{ m}^2/\text{g}$). The Raman spectra of titania supported vanadia catalysts as a function of vanadium oxide loading reveals the presence of three different vanadia species on the TiO_2 support under *in situ* dehydrated conditions [19]. At low loadings (*ca.* 1 wt.% V_2O_5), a single sharp band is present at *ca.* 1030 cm^{-1} which is due to an isolated four coordinated surface vanadium oxide species containing one terminal V=O bond and three bridging V–O–Ti bonds [20]. At intermediate loadings (2–6 wt.% V_2O_5), a second band is present at *ca.* 930 cm^{-1} which has been assigned to a polymerized, four coordinated surface vanadium oxide species [20]. At high loadings (>6 wt.% V_2O_5), a third sharp band is present at 994 cm^{-1} due to crystalline V_2O_5 [20] which indicates that the close-packed surface vanadium oxide monolayer has been formed and essentially all the reactive surface hydroxyls consumed. A similar behavior is also observed for the surface vanadium oxide species on other oxide supports. Furthermore, different surface metal oxide species (molybdenum oxide [8] and chromium oxide [16]) also show similar behavior with respect to the forma-

tion of isolated, polymeric, and bulk metal oxide phases. Surface rhenium oxide species is an exception since it does not form polymerized species or bulk/crystalline Re_2O_7 on oxide supports [14]. Thus, the catalyst composition is a critical parameter since it influences the formation of different metal oxide structures.

The reactivity of the titania supported metal oxide (Re, Cr, Mo, and V) catalysts was probed by the methanol oxidation reaction to study the effect of surface metal oxide coverages. The oxidation of methanol over the titania supported vanadia catalysts exclusively yield formaldehyde, 95%+, as the reaction product. The titania support in the absence of surface vanadia yielded dimethyl ether and trace amounts of CO_2 . The almost complete formation of formaldehyde demonstrates that the reactivity of the titania supported vanadia catalysts is due to the surface vanadia redox sites. The reactivity, measured in terms of turnover number (TON), is approximately constant, $2.0 \pm 0.7 \text{ s}^{-1}$, for less than monolayer coverages. In comparison, the TON of bulk V_2O_5 is two orders of magnitude less than the titania supported vanadia catalysts [12] indicating that crystalline V_2O_5 is significantly less active than surface vanadia species for redox reactions. The reactivity of the different titania supported metal oxide species was also obtained and plotted *versus* the metal oxide loading in Fig. 6. Figure 6 shows that for the titania supported vanadium oxide, rhenium oxide, molybdenum oxide, and chromium oxide catalysts, the reactivity (TON) is approximately constant as a function of surface coverage, and varies within the limits of $(1.1 \text{ to } 2.7) \text{ s}^{-1}$, $(0.9 \text{ to } 1.2) \text{ s}^{-1}$, $(0.2 \text{ to } 0.6) \text{ s}^{-1}$, and $(0.1 \text{ to } 0.3) \text{ s}^{-1}$ for the $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{Re}_2\text{O}_7/\text{TiO}_2$, $\text{MoO}_3/\text{TiO}_2$, and $\text{CrO}_3/\text{TiO}_2$

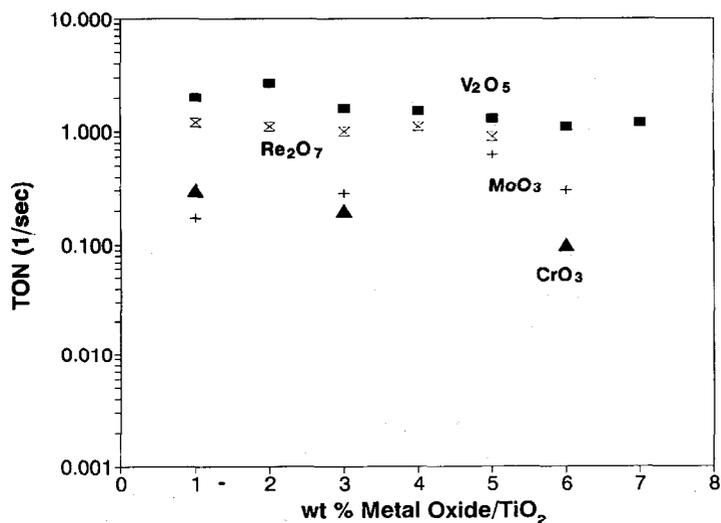


Fig. 6. The methanol oxidation TON of supported metal oxide catalysts as a function of metal oxide loading.

TiO₂ systems, respectively. Thus, the reactivity of surface metal oxide species is practically independent of surface coverage and structure for methanol oxidation.

To study the effect of the synthesis method for forming metal oxide monolayers a series of V₂O₅/TiO₂ catalysts was prepared by different methods: equilibrium adsorption, vanadium oxalate, vanadium alkoxides and vanadium oxychloride grafting. The *in situ* dehydrated Raman spectra of all these catalysts exhibit a sharp band at ca. 1030 cm⁻¹ characteristic of the isolated surface vanadium oxide species [21]. Thus, the synthesis method does not affect the final structure of the surface vanadium oxide species on titania. Similar conclusions were also found for molybdenum oxide supported on silica [11], titania [21], and alumina [22]. Reactivity studies using the methanol oxidation reaction on these vanadia–titania catalysts show essentially identical turnover numbers. Consequently, the preparation method is not a critical parameter since it does not influence the structure of the surface metal oxide species or its reactivity.

There have been claims in the literature that the modification or structure of the oxide support is critical for obtaining a good catalyst [23]. To investigate this issue a series of V₂O₅/TiO₂ catalysts were prepared on different TiO₂ support structures (anatase, rutile, anatase + rutile, anatase + brookite, and B) [24]. *In situ* Raman characterization revealed that the same surface vanadia species were present on all the different titania supports since a Raman band at 1024–1031 cm⁻¹ was observed for these vanadia–titania catalysts. The dehydrated solid state ⁵¹V NMR powder pattern shows a similar shift in the –660 to –670 ppm region confirming the presence of the same surface vanadia species. The reactivity of these different titania supported vanadia catalysts was probed with methanol oxidation and found to be identical with a TON of 2.1 ± 0.5 sec⁻¹ and is shown in Fig. 7. Thus, the combined structure and reactivity information shows that the structure or modification of the ox-

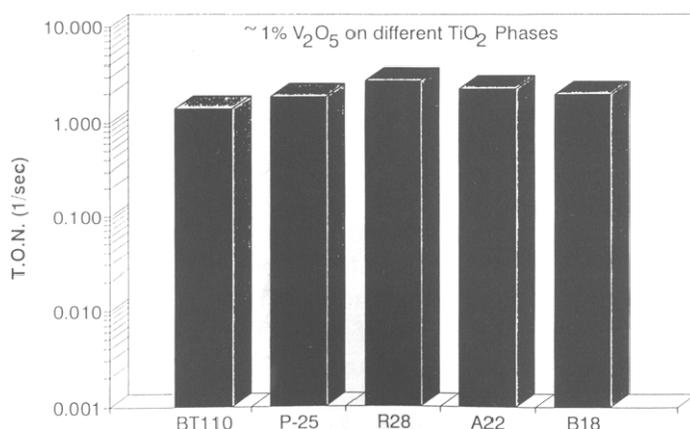


Fig. 7. The methanol oxidation TON of surface vanadium oxide phase as a function of the structure of the titania support. See experimental section for titania support nomenclature.

oxide support does not affect the surface metal oxide structure or the catalyst reactivity.

The nature of the supported metal oxide phase can also be influenced by the calcination temperature. Moderate calcination temperatures, 350–500°C, are required to decompose the metal oxide precursors (oxalates, alkoxides, oxychlorides, *etc.*) and/or evaporate the solvents used during preparation to form the surface metal oxide species [25]. Insufficient calcination temperatures (usually less than 300°C) do not completely decompose the precursors or remove the solvents. In contrast, high calcination temperatures (greater than 600°C) can result in shrinking of the surface area of the oxide support. Decreasing the available surface area for the surface metal oxide species, increases the surface coverage of the metal oxide species and, in severe cases (of high calcination temperatures), destroys the surface metal oxide phase and form bulk metal oxide phases or even solid state solutions [25–27]. Thus, calcination temperature is an important parameter that controls the activation and deactivation of supported metal oxide catalysts. However, supported metal oxide catalysts are typically prepared by calcining at 350–500°C which eliminate problems associated with activation and deactivation.

Conclusions

The above discussion demonstrates that it is possible to molecularly design supported metal oxide catalysts with the assistance of molecular characterization methods such as Raman spectroscopy and chemical probes such as the methanol oxidation reaction. The formation and location of the surface metal oxide species are controlled by the surface hydroxyl chemistry, and the surface metal oxide species are located in the outermost layer of the catalysts as an overlayer. The specific oxide support and the specific surface metal oxide are critical parameters since they dramatically affect the reactivity of the surface metal oxide species, but the structure of the oxide support has no effect on the surface metal oxide structure and reactivity. The reactivity is related to the M–O-support bond strength. The catalyst composition (surface metal oxide coverage) is a critical parameter since it affects the presence of different metal oxide species (isolated surface species, polymerized surface species, and crystalline phases). The reactivity, TON, of the surface metal oxide phase is apparently independent of surface metal oxide coverage for the molecularly dispersed metal oxide phases and is very different from that of the crystalline metal oxide phases. The preparation method is not a critical parameter since it does not influence the structure or reactivity of the surface metal oxide species. Calcination temperature is an important parameter since it controls the activation and deactivation of supported metal oxide catalysts, but calcination temperature is not critical if moderate temperatures, 350–500°C, are used. In summary, the critical parameters that affect the catalytic properties of sup-

ported metal oxide catalysts are the specific oxide support and the specific surface metal oxide.

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