In situ Raman spectroscopy studies of catalysts

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In situ Raman spectroscopy is rapidly becoming a very popular catalyst characterization method because Raman cells are being designed that can combine *in situ* molecular characterization studies with simultaneous fundamental quantitative kinetic studies. The dynamic nature of catalyst surfaces requires that both sets of information be obtained for a complete fundamental understanding of catalytic phenomena under practical reaction conditions. Several examples are chosen to highlight the capabilities of *in situ* Raman spectroscopy to problems in heterogeneous catalysis: the structural determination of the number of terminal M=O bonds in surface metal oxide species that are present in supported metal oxide catalysts; structural transformations of the MoO_3/SiO_2 and MoO_3/TiO_2 supported metal oxide catalysts under various environmental conditions, which contrast the markedly different oxide–oxide interactions in these two catalytic systems; the location and relative reactivity of the different surface $M–OCH_3$ intermediates present during CH_3OH oxidation over V_2O_5/SiO_2 catalysts; the different types of atomic oxygen species present in metallic silver catalysts and their role during CH_3OH oxidation to H_2CO and C_2H_4 epoxidation to C_2H_4O; and information about the oxidized and reduced surface metal oxide species, isolated as well as polymerized species, present in supported metal oxide catalysts during reaction conditions. In summary, *in situ* Raman spectroscopy is a very powerful catalyst characterization technique because it can provide fundamental molecular-level information about catalyst surface structure and reactive surface intermediates under practical reaction conditions.

Keywords: Raman, *in situ* spectroscopy, catalysts, metal oxides, molecular structures, selective oxidation reactions

1. Introduction

Raman spectroscopy is among the handful of catalyst characterization techniques that can provide molecular-level information about heterogeneous catalysts under *in situ* controlled environmental conditions (temperature, partial pressures of the gas phase components, etc.) [1]. The combination of fundamental molecular structural information and *in situ* capabilities has resulted in an explosion of Raman spectroscopy characterization studies in the catalysis literature (see figure 1). Twenty years ago only a handful of Raman spectroscopy publications appeared in the catalysis literature and none were *in situ* studies. In the past few years, more than 100 Raman characterization publications have appeared annually in the catalysis literature and a significant fraction of the papers were performed under *in situ* conditions (about 20–40 publications/year). Presently, the total number of Raman spectroscopy studies that have appeared in the catalysis literature amount to 1322 publications of which 221 are *in situ* studies. These *in situ* Raman studies have demonstrated the dynamic nature of heterogeneous catalyst surfaces and the importance of performing characterization studies under reaction conditions.

Several recent publications have extensively surveyed the Raman studies that have appeared in the heterogeneous catalysis literature [2–6]. Consequently, the purpose of this paper is only to illustrate the type of fundamental information that can be obtained from *in situ* Raman studies of heterogeneous catalysts. The examples will be taken from the author's research laboratory where much of the work has focused on supported metal oxide catalysts and oxidation reactions. The examples selected will address the following topics: (1) molecular structural determinations, (2) structural transformations of surface metal oxides, (3) surface reaction intermediates and (4) reduction of surface metal oxide species during oxidation reactions.

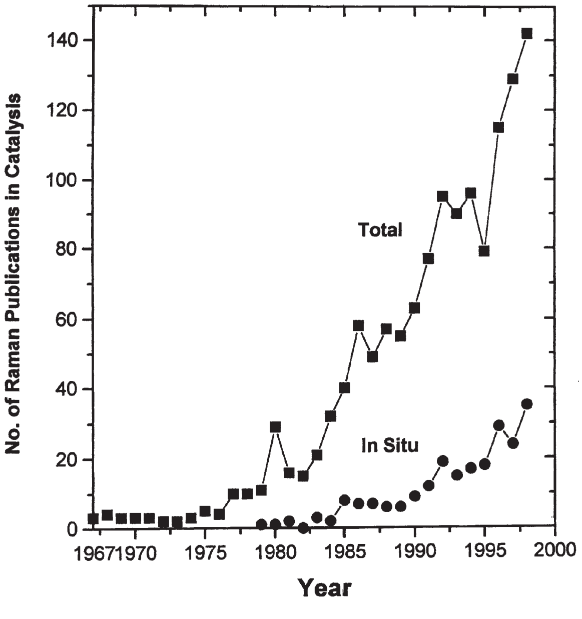


Figure 1. Number of Raman publications in catalysis.

2. *In situ* Raman cells

The major limitation to performing *in situ* Raman studies is the lack of commercially available *in situ* Raman cells. This has resulted in the design of *in situ* Raman cells that have become more sophisticated with time. One of the initial *in situ* Raman cells was designed by Wang

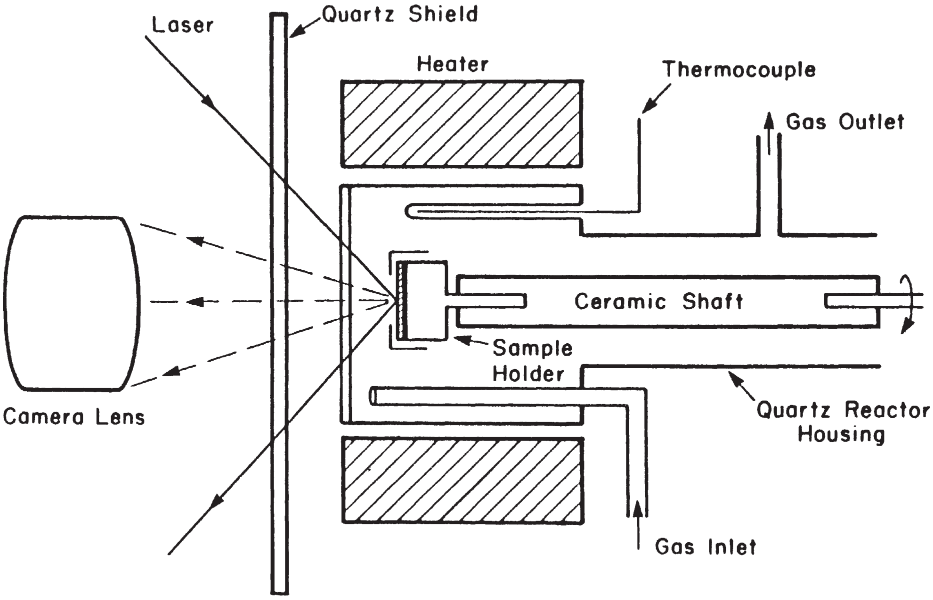
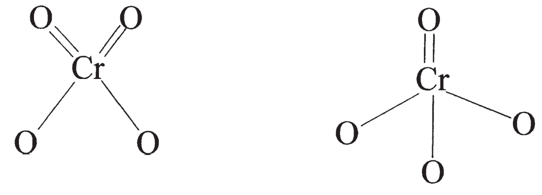


Figure 2. Rotating *in situ* Raman cell.

and Hall [7]. The cell contained a self-supporting catalyst wafer attached to a stationary rod that could be cooled to sub-ambient temperatures with liquid nitrogen. Such an *in situ* Raman cell was satisfactory for the investigation of ambient (hydrated) and dehydrated catalyst samples. However, the stationary feature of this design resulted in potential problems due to local heating of the catalyst sample by the focused laser beam (e.g., laser-induced dehydration, photocatalysis and sample damage in rare cases). In order to minimize local heating effects, *in situ* Raman cells were developed that could be rotated at up to ~2000 rpm (see figure 2) [8,9]. These designs also employed self-supporting catalyst wafers, which caused significant gas bypassing around the catalyst wafer as well as potential internal mass transfer limitations. Thus, only the exterior region of the catalyst wafer primarily participates in the catalytic reaction since there is no driving force to push the flowing gases through such a pressed porous catalyst wafer. Fortunately, the Raman signal also originates from the exterior region of the catalyst wafer because of its limited sampling depth (~1 μm), and the Raman signal is essentially sampling the reaction region. However, simultaneous fundamental kinetic studies are difficult to perform with catalyst wafers because of their inherent mass transfer limitations. In an attempt to get around this problem, Volta et al. designed a stationary cell with gas flow through loose catalyst powder and employed a rotating laser beam [10]. The advantage of this cell design is that the reactive gas flows through the loose catalyst powder, but the arrangement employed does not result in plug flow conditions and there is significant back-mixing due to the open empty space above the loose powder. Thus, fundamental kinetic data are not readily obtained in such a system. Liao et al. designed a moving *in situ* Raman cell where quantitative fundamental kinetics are achievable [11]. In their design, the reactive gas flows through a loose powder and the cell moves up and down in order not to hold the laser beam in one spot during the analysis. The advantage of this arrangement is that plug flow through a packed catalyst bed is achieved and, therefore, fundamental quantitative kinetics and *in situ* Raman data about the catalyst can be simultaneously obtained. The disadvantage is the complexity of such a system. No data from such a system have yet been appeared in the catalysis literature. The current trend to simultaneously monitor the catalyst and obtain fundamental quantitative kinetics will result in further improvements in the design of *in situ* Raman cells in the coming years.

3. Molecular structural determinations

Supported metal oxide catalysts are extensively employed in the petroleum, chemical and environmental industries [12]. Such catalysts consist of two-dimensional metal oxide overlayers (e.g., oxides of Re, Cr, Mo, W, V, Nb, etc.) on high surface area oxide supports (e.g., alumina, titania, silica, etc.) [6]. In the case of supported chromia catalysts, the number of terminal Cr=O bonds present in the surface chromia species has been debated in the literature (see figure 3) [13]. The surface chromate species may contain one terminal Cr=O bond and



ν_s (Cr = O), ν_{as} (Cr = O) ν_s (Cr = O)

Figure 3. Proposed structures for surface chromate species.

three single Cr–O bonds (mono-oxo structure) or two terminal Cr=O bonds and two single Cr–O bonds (di-oxo structure). The single bonds may be connected to neighboring surface chromate species or to the oxide support cations. Oxygen-18 exchange studies clearly revealed that only mono-oxo surface chromate species are present in supported metal oxide catalyst since only two vibrations due to $Cr{=}^{16}O$ and $Cr{=}^{18}O$ were detected. The di-oxo structure would be expected to give rise to three vibrations due to $^{16}O{=}Cr{=}^{16}O$, $^{18}O{=}Cr{=}^{18}O$ and $^{16}O{=}Cr{=}^{18}O$. This conclusion was further supported by combined *in situ* Raman and IR studies since the vibrational selection rules dictate that mon-oxo structures should possess coincident IR and Raman vibrations and that di-oxo structures should possess IR and Raman vibrations that are separated by 20–30 cm^{-1} (IR(asymmetric Cr=O) $>$ Raman (symmetric Cr=O)). *In situ* Raman studies during butane dehydrogenation further revealed that both isolated and polymerized surface mono-oxo chromate species coexisted in the supported chromium oxide catalyst and that the polymerized surface chromate species was preferentially reduced under reducing conditions. Analogous oxygen-18 *in situ* Raman studies demonstrated that other surface metal oxide overlayers also possess mono-oxo structures (e.g., surface oxides of Mo, W, V and Nb) [14].

4. Structural transformations of surface metal oxides

The surfaces of metal oxide catalysts are very dynamic and readily respond to the reaction environment [15]. This is even more evident for supported metal oxide catalysts, where two-dimensional surface metal oxide species are present. Supported MoO_3/SiO_2 catalysts undergo numerous structural transformations that depend on temperature and gaseous environment (see figure 4) [16,17]. Under ambient conditions and room temperature, the surface molybdenum oxide species are present as hydrated Mo_7O_{24} clusters (main Raman bands at 941 and 867 cm^{-1}) due to the presence of adsorbed ambient moisture. Introduction of additional adsorbed mositure, by flowing saturated air over the catalyst, converts the hydrated Mo_7O_{24} cluster to $H_4SiMo_{12}O_{40}$ (silicomolybdic acid heteropolyoxoanion, main Raman bands at 975 and 955 cm^{-1}). Upon dehydration at elevated temperature, these molybdate clusters are decomposed to isolated surface molybdenum oxide species possessing one terminal Mo=O bond and four bridging Mo–O–Si bonds (main Raman band 980 cm^{-1}). Exposure of the dehydrated surface molybdenum oxide species to methanol oxidation at 230 °C converts the surface molybdenum oxide species to crystalline beta-MoO_3 (main Raman bands at 843 and 770 cm^{-1}). The beta-MoO_3 crystallites are not thermally stable and convert above 300 °C to alpha-MoO_3 crystallites (main Raman bands at 991 and 816 cm^{-1}). These structural transformations have a very significant effect on the activity and selectivity of methanol oxidation over MoO_3/SiO_2 catalysts. The isolated surface Mo oxide species is active and selective for the formation of $HCOOCH_3$, while the crystalline MoO_3 phases are much less active and are selective for the formation of H_2CO.

In contrast to the MoO_3/SiO_2 catalyst system, where the interaction between MoO_3 and SiO_2 is very weak, the strong interaction between MoO_3 and TiO_2transforms crystalline MoO_3 to surface molybdenum oxide species on the TiO_2 support during methanol oxidation at 230 °C [18]. This transformation is due to the formation of surface Mo–OCH_3 intermediate species (main Raman band at 969 cm^{-1}) that transport the Mo from the crystalline MoO_3 phase to the TiO_2 support. The driving force for this reaction induced spreading is the much stronger interaction of Mo with the titania support surface hydroxyls compared to the weak cohesive interaction in the layered alpha-MoO_3 crystalline structure. This three-dimensional to two-dimensional structural transformation is accompanied by a significant change in the catalytic activity of the MoO_3/TiO_2 catalyst system. The methanol oxidation catalytic activity continuously increases until all the crystalline MoO_3 particles are converted to surface Mo species on the titania support. This experiment again reveals that the surface molybdenum oxide species are more active than the crystalline MoO_3 phase for methanol oxidation. Furthermore, the temperatures at which these structural transformation occur are significantly below the Tammann temperature of crystalline MoO_3, indicating that thermal spread-

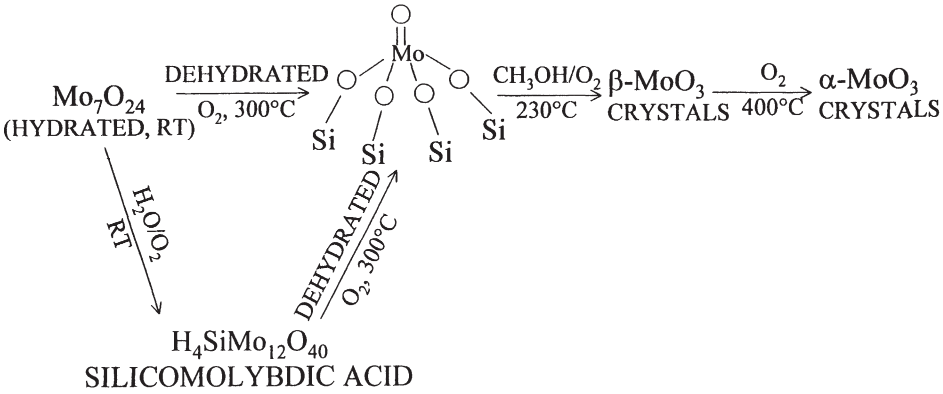


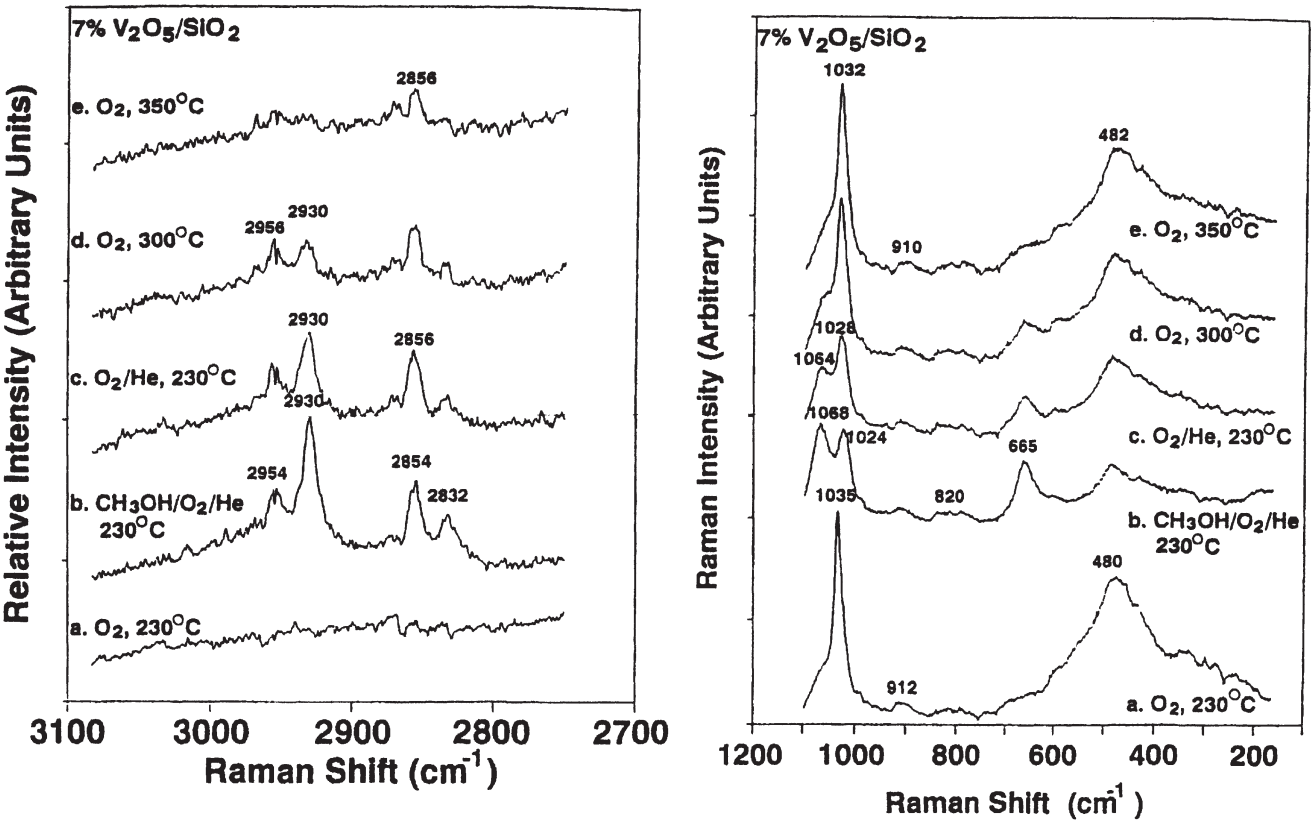
Figure 4. Structural transformations for the MoO_3/SiO_2 catalyst system.

ing is not involved during this reaction induced spreading.

5. Surface reaction intermediates

It is well documented that surface methoxy intermediates, CH_3O_{ads}, are present on oxide surfaces during methanol oxidation [19]. For supported metal oxide catalysts such surface methoxy intermediates may coordinate to the surface metal oxide species as well as the oxide support [20]. For example, during methanol oxidation over V_2O_5/SiO_2 catalysts, both surface V–OCH_3 (main methyl vibrations at 2930 and 2832 cm^{-1}) and surface Si–OCH_3 (main methyl vibrations at 2954 and 2854 cm^{-1}) intermediates are detected by Raman spectroscopy (see figure 5(a)). In addition, V–O vibrations are observed at 665 cm^{-1}and C–O vibrations are observed at 1068 cm^{-1} due to the V–OCH_3 complex (see figure 5(b)). Formation of the V–OCH_3 intermediates causes a significant decrease in the terminal V=O bond vibration and shifts the Raman band from 1035 to 1024 cm^{-1} (see figure 5(b)). As the temperature is increased in an oxygen environment, the V–OCH_3 intermediates decompose faster than the Si–OCH_3 intermediates (see figure 5(a)). This suggests that the V–OCH_3 intermediates are the active surface intermediates and that the Si–OCH_3 intermediates are just spectator species during methanol oxidation. Corresponding temperature programmed reaction spectroscopy (TPRS) studies showed that the V–OCH_3 intermediates are oxidized to H_2CO at ∼300 °C and that the Si–OCH_3 intermediates decompose to CO and CH_4 at ∼400 °C. The relative ratio of V–OCH_3/Si–OCH_3 species increases with the surface vanadia coverage. For catalyst systems that possess a complete monolayer of surface metal oxide species, there are no surface methoxy vibrations due to the underlying oxide support. This observation is consistent with the formation of a complete two-dimensional surface metal oxide overlayer in supported metal oxide catalysts under *in situ* reaction conditions [21].

Silver catalysts are extensively employed in industry for methanol oxidation to formaldehyde, ethylene epoxidation and, more recently, for butadiene epoxidation [22]. The nature of the oxygen intermediates in silver catalysts has not been clarified in the catalysis literature. Recent *in situ* surface enhanced Raman spectroscopy (SERS) studies of oxygen species on silver have shown that only atomic oxygen species are present in silver catalysts during oxidation catalysis: surface Ag=O (Raman vibration at 956 cm^{-1}), sub-surface Ag–O–Ag (Raman vibration at 800 cm^{-1}) and bulk Ag_nO (Raman vibration at 600–700 cm^{-1}) [23,24]. The atomic nature of the various oxygen species was readily verified by isotopic oxygen-18 experiments, which



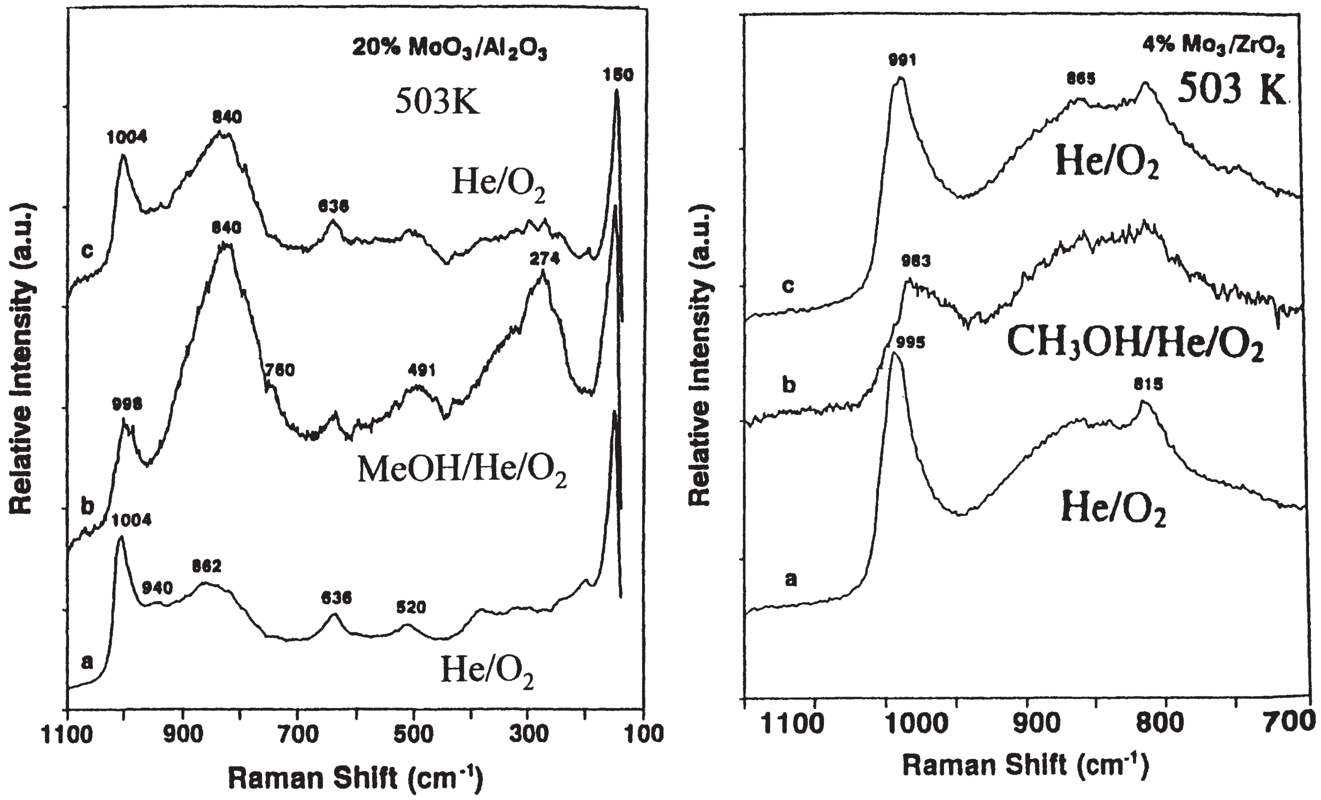
(a) (b)

Figure 5. *In situ* Raman spectra of V_2O_5/TiO_2 catalysts during methanol oxidation: (a) the methoxy vibrational region from 2700–3100 cm^{-1}; (b) the metal–oxygen vibrational region from 100–1200 cm^{-1}.

only revealed two vibrations for each oxygen species (e.g., 956 cm^{-1} for atomic ^{16}O and 932 cm^{-1} for atomic ^{18}O and no vibrations were detected for $^{16}\mathrm{O}^{18}\mathrm{O}$ molecular species) [24]. Molecularly adsorbed oxygen species on the silver surface has only been observed at sub-ambient temperatures. *In situ* Raman studies during methanol and ethylene oxidation, employing gas phase $^{16}\mathrm{O}_2$ and oxygen-18 labeled surface atomic oxygen species, were performed to obtain additional insight into the oxygen species involved in these reactions. The *in situ* Raman measurements revealed that the surface Ag=O atomic oxygen species is very stable during these reactions and that the sub-surface Ag–O–Ag atomic oxygen species is preferentially consumed during these oxidation reactions [24]. Thus, the sub-surface atomic oxygen species, Ag–O–Ag, is the reactive atomic oxygen intermediate responsible for these oxidation reactions over silver catalysts and adsorbed molecular oxygen is not involved in these selective oxidation reactions over silver catalysts under practical reaction conditions.

6. Reduction of surface metal oxide species during oxidation reactions

During oxidation reaction over some supported metal oxide catalysts, the surface metal oxide species become partially reduced during these redox reactions and can be directly monitored with *in situ* Raman spectroscopy. The *in situ* Raman spectra during methanol oxidation over a 20% $\mathrm{MoO_3/Al_2O_3}$ catalyst are shown in figure 6(a) [25]. Prior to methanol oxidation, the dehydrated and fully oxidized surface molybdenum oxide species, Mo^{6+}, gives rise to major Raman bands at 1004, 862, 636 and 520 cm^{-1}. These Raman vibrations are associated with the symmetric stretch of the terminal Mo=O bond, the symmetric stretch of O–Mo–O functionality, and the asymmetric and symmetric stretches of the bridging Mo–O–Mo bond, respectively. Exposure of the 20% $\mathrm{MoO_3/Al_2O_3}$ catalyst to methanol oxidation conditions significantly reduces the Mo=O vibration at ~1000 cm^{-1} and creates new strong Raman bands at 840, 491 and 274 cm^{-1}, which are due to the reduced surface Mo^{4+} species. The molecular structure of this reduced surface Mo^{4+} species has not been determined by any spectroscopic methods at present. Reoxidation of the reduced 20% $\mathrm{MoO_3/Al_2O_3}$ catalyst significantly decreases the Raman vibrations associated with the reduced surface Mo^{4+} species, and additional oxidation at higher temperatures completely reoxidizes the reduced surface Mo^{4+} species to the initial surface Mo^{6+} species present prior to the methanol oxidation reaction. An analogous series of *in situ* Raman experiments are shown in figure 6(b) for methanol oxidation over a 4% $\mathrm{MoO_3/ZrO_2}$ catalyst [25]. Prior to methanol oxidation, the dehydrated and fully oxidized surface molybdenum oxide species, Mo^{6+}, gives rise to major Raman bands at 995, 865 and 815 cm^{-1}.



(a) (b)

Figure 6. *In situ* Raman spectra of Mo^{4+} species during methanol oxidation: (a) 20% $\mathrm{MoO_3/Al_2O_3}$; (b) 4% $\mathrm{MoO_3/ZrO_2}$.

These Raman vibrations are associated with the symmetric stretch of the terminal Mo=O bond, the symmetric stretch of the O–Mo–O functionality, and the presence of a trace of crystalline MoO_3, respectively. Exposure of the 4% MoO_3/ZrO_2 catalyst to methanol oxidation conditions significantly reduces the Mo=O vibration and shifts the band from 995 to 983 cm^{-1}. The reduction in intensity and shift in frequency are related to the reduction of the surface Mo^{6+} species and formation of Mo–OCH_3 intermediates. In contrast to the MoO_3/Al_2O_3 catalyst, the appearance of strong Raman bands due to reduced surface Mo species is not observed for the MoO_3/ZrO_2 catalyst during methanol oxidation. The absence of strong Raman bands for reduced surface Mo species on ZrO_2 suggests that a different surface Mo oxide structure or oxidation state is present for this system. Unfortunately, strong Raman bands for reduced surface Mo species are only observed for the MoO_3/Al_2O_3 system and not for any of the other supported molybdenum oxide catalysts. In the case of supported vanadia and chromia catalysts, no new Raman bands were observed for the reduced surface metal oxide species [21,26]. Thus, it appears that most reduced surface metal oxide species do not give rise to strong Raman bands.

In situ Raman studies do provide information about the relative reduction characteristics of the fully oxidized isolated and polymerized surface metal oxide species during redox reactions. It appears that the polymerized surface metal oxide species, possessing bridging M–O–M bonds, are preferentially reduced relative to isolated surface metal oxide species [21,26,27]. Quantitative estimation of the extent of reduction cannot be determined because sample darkening, from reduction in oxidation state and carbon deposition, may result in nonlinear, and occasionally unreliable, changes in the Raman intensity. There does not, however, appear to be a relationship between the extent of reduction of the surface metal oxide species and the activity and selectivity of supported metal oxide catalysts during oxidation reactions [28]. Recent *in situ* UV-Vis diffuse reflection spectroscopy (DRS) studies have revealed that the surface oxide species are predominantly in their fully oxidized state during practical oxidation reaction conditions [29]. Furthermore, temperature programmed reaction spectroscopy (TPRS) and TAP studies have demonstrated that the oxidized surface metal oxide species are more active than the reduced surface metal oxide species for oxidation reactions [30,31].

7. Conclusions

Raman spectroscopy is a very powerful catalyst characterization technique because it can provide fundamental molecular-level information about catalyst surface structures and reaction intermediates. This has resulted in an exponential growth in the application of Raman spectroscopy to catalyst characterization over the past two decades. *In situ* Raman spectroscopy is rapidly becoming a very popular catalyst characterization method because Raman cells are being designed that can combine *in situ* characterization studies with simultaneous fundamental quantitative kinetic studies. The dynamic nature of catalyst surfaces requires that both sets of information be obtained for a full fundamental understanding of catalytic phenomena under practical reaction conditions.

The above survey of the capabilities of *in situ* Raman spectroscopy of heterogeneous catalysts demonstrated that (1) the molecular structures of surface metal oxide species can be directly determined, (2) the two-dimensional metal oxide structural transformations can be readily monitored, (3) the nature and surface location of surface reaction intermediates can be readily identified and (4) the polymerized surface metal oxide species are more reducible than isolated surface metal oxide species and (5) most reduced surface metal oxide species do not give rise to strong Raman bands.

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References

[1] J.M. Thomas and W.J. Thomas, *Principles and Practice of Heterogeneous Catalysis* (VCH, New York, 1997).
[2] J.R. Bartlett and R.P. Cooney, in: *Spectroscopy of Inorganic-Based Materials*, eds. R.J.H. Clark and R.E. Hester (Wiley, New York, 1987) p. 187.
[3] J.M. Stencel, *Raman Spectroscopy for Catalysis* (Van Nostrand, New York, 1990).
[4] M. Mehicic and J.G. Grasselli, in: *Analytical Raman Spectroscopy*, eds. J.G. Grasselli and B. Bulkin (Wiley, New York, 1991).
[5] I.E. Wachs, and F.D. Hardcastle, in: *Catalysis – A Specialist Periodical Report*, Vol. 10 (Royal Society of Chemistry, Cambridge, UK, 1993) pp. 102–153.
[6] I.E. Wachs, Catal. Today 27 (1996) 437.
[7] L. Wang and W.K. Hall, J. Catal. 66 (1980) 276; 77 (1982) 232; 83 (1983) 242.
[8] I.E. Wachs, F.D. Hardcastle and S.S. Chan, Spectrosocpy 1 (1986) 30.
[9] Q. Sun, J.-M. Jehng, H. Hu, R.G. Herman, I.E. Wachs and K. Klier, J. Catal. 165 (1997) 91.
[10] J.C. Volta, in: *Catalytic Selective Oxidation*, eds. T.S. Oyama and J. Hightower, ACS Symp. Ser. 523, Washington, DC, 1993.
[11] Y.-Y. Liao, P-.F. Hong and J.-X. Cai, in: *Proc. XIVIII Intern. Conference On Raman Spectroscopy*, eds. N.T. Yu and X.Y. Li, Hongkong, 1994, pp. 1086–1090.
[12] C.L. Thomas, *Catalytic Processes and Proven Catalysts* (Academic Press, New York, 1970).
[13] B.M. Weckhuysen and I.E. Wachs, J. Phys. Chem. B 101 (1997) 2793.

[14] B.M. Weckhuysen, L.J. Burcham and I.E. Wachs, to be published.

[15] J. Haber, Studies in Surf. Sci. and Catal. 110 (1997) 1.

[16] M.A. Banares, H. Hu and I.E. Wachs, J. Catal. 150 (1994) 407; 155 (1995) 249.

[17] M. de Boer, A.J. van Dillen, D.C. Koningsberger, M.A. Vuurman, I.E. Wachs and J.G. Geus, Catal. Lett. 11 (1991) 227.

[18] Y. Cai, C.-B. Wang and I.E. Wachs, Studies in Surf. Sci. and Catal. 110 (1997) 255.

[19] U. Chowdhry, A. Ferretti, L.E. Firment, C.J. Machiels, F. Ohuchi, A.W. Sleight and R.H. Staley, Appl. Surf. Sci. 19 (1984) 360.

[20] J.-M. Jehng, H. Hu, X. Gao and I.E. Wachs, Catal. Today 28 (1996) 335.

[21] G. Deo, L.J. Burcham and I.E. Wachs, to be published.

[22] J.R. Monnier, Studies in Surf. Sci. and Catal. 110 (1997) 135.

[23] D. Herein, H. Werner, T. Scedel-Niedrig, T. Neisius, A. Nagy, S. Bernd and R. Schlögl, Studies in Surf. Sci. and Catal. 110 (1997) 103.

[24] C.-B. Wang, G. Deo and I.E. Wachs, J. Phys. Chem. B, submitted.

[25] H. Hu and I.E. Wachs, J. Phys. Chem. 99 (1995) 10911.

[26] B.M. Weckhuysen and I.E. Wachs, J. Phys. Chem. 100 (1996) 14437.

[27] I.E. Wachs, J.-M. Jehng, G. Deo, B.M. Weckhuysen, V.V. Guliants, J.B. Benziger and S. Sundaresan, J. Catal. 170 (1997) 75.

[28] I.E. Wachs, G. Deo, J.-M. Jehng, D.S. Kim and H. Hu, in: *Heterogenous Hydrocarbon Oxidation*, ACS Symp. Ser. 638, eds. B.K. Warren and S.T. Oyama (Am. Chem. Soc., Washington, DC, 1996) pp. 292–299.

[29] X. Gao and I.E. Wachs, to be published.

[30] L.E. Briand, W. Farneth and I.E. Wachs, to be published.

[31] D.S. Lafyatis, G. Creten and G.F. Froment, Appl. Catal. A: General 120 (1994) 85.