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In situ Raman spectroscopy. A powerful tool for studies in selective catalytic oxidation

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Abstract

In this review, some of advantages and problems of in situ Raman spectroscopy are briefly mentioned. The applications of laser Raman spectroscopy LRS to the study of catalysts used for selective oxidation is then reviewed based on published work on catalysis by molybdate and VPO catalysts. Investigations of synergy effects have also been carried and results on ^{18}O-exchange and reoxidation of SbO_x/MoO_3 physical mixtures are reported. Spillover oxygen – if present – could not be detected.

Peroxide species have been detected on working methane coupling catalysts at temperatures up to 1070 K and they have been identified as centers for the activation of methane.

Model studies were performed of the methanol oxidation to formaldehyde on Ag single crystal surface at temperatures up to 1170 K. Surface enhancement permitted the detection of a strongly chemisorbed surface oxygen species O_γ, which was in equilibrium with a bulk species O_β and which was identified as the reactive species involved in the methanol oxidation.

Keywords: Raman spectroscopy; Selective catalytic oxidation

1. Introduction

Photon in/photon out techniques are particularly suitable for in situ investigations of catalytic systems. Vibrational spectroscopies, such as infrared transmission and diffuse reflectance spectroscopies and laser Raman spectroscopy LRS, and X-ray absorption spectroscopy XAS have to be mentioned here. Among the vibrational spectroscopies, for in situ application in selective catalytic oxidation under even extreme temperature conditions, LRS is particularly useful for several reasons that will be briefly outlined in this article. Several review articles on LRS as applied to catalysis research have been published in recent years [1–5]. Therefore a general introduction to the technique will not be given here. The special value of in situ LRS for investigations in selective catalytic oxidation will be detailed on the basis of several examples. It will first be demonstrated that a phase analysis of the solid catalyst under reaction conditions can be performed. The solid state spectroscopy also permits the detection of incorporation of ^{18}O isotopic labels and it can be applied to study synergy effects in complex oxide mixtures. In situ LRS can also be used to detect and analyze chemisorbed species and possible catalytic intermediates. Thus, peroxide ions have been detected in working methane

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coupling catalysts at temperatures up to 1070 K. In the final example, it will be shown that surface enhancement even permits in situ LRS studies on model Ag single crystal surfaces. Having chosen these examples, the author hopes to illustrate the broad spectrum of possible applications of in situ LRS in research on selective catalytic oxidation.

2. Raman spectroscopy. Advantages and problems

Laser Raman spectroscopy (LRS) provides several advantages for in situ-application when compared to Fourier transform IR (FTIR) spectroscopy in the transmission mode:

1. Many materials of catalytic importance, including the most frequently used support oxides silica, alumina and titania have relatively ionic metal–oxygen bonds. They are therefore opaque in the infrared region at wavenumbers typically below 1200 cm^{-1}. This wavenumber regime is accessible to LRS even with TiO_2 which has but a few relatively narrow Raman active vibrational modes below 700 cm^{-1}. Vibrational spectra of supported active phases (e.g. molybdena/alumina or vanadia/titania) and of chemisorbed species can thus be recorded.
2. Catalytic systems can be studied by LRS under extreme pressure and temperature conditions. This is due to the fact that the cell design is usually relatively less demanding for LRS than for in situ-FTIR spectroscopy. In addition, high temperature FTIR spectroscopy is limited by the sample emission which is not a problem in LRS when the excitation (and hence the detection) occurs in the visible.
3. Although very many different cell designs have been described in the literature, in situ Raman cells are typically simpler than in situ-FTIR cells. When excitation in the UV or visible region is applied, simple quartz cells with quartz windows can be used (see, for example, [6], where a quartz cell is described that was used for in situ studies of working methane coupling catalysts (vide infra)).
4. The sample morphology does not play any significant role, and particularly thin self-supporting wafers which are required for transmission FTIR and which are sometimes difficult to make, are not necessary for LRS.
5. Spatial resolution $< 10^{-2}$ cm can be achieved by LRS simply because the laser beam has to be focused onto the sample surface [7]. Even better spatial resolution (ca. 20–30 μm) can be reached when a Raman microscope is used [8].

Besides these important advantages of LRS, the experimentalist will, however, also face problems which in unfavourable cases will make it impossible to record Raman spectra of catalytic materials. Some of these problems are listed below.

1. The intrinsic low Raman scattering cross sections (typically lower by a factor 10^{-6} than the Rayleigh scattering) may lead to severe sensitivity limitations.
2. Quantitation is practically impossible since scattering cross sections of surface species are unknown and the actual scattering volume from pressed powder samples remains unknown as well.
3. Although the sample temperature can be measured, the temperature of the sample within the laser focus is usually not known. This temperature may be determined from the Stokes and anti-Stokes line intensities via the Boltzmann-factor although this procedure is not trivial either.
4. There may be significant laser heating which can lead to sample degradation. Therefore, LRS of catalysts should always be carried out at the lowest possible laser power. Also, cells have been designed for in situ studies in which the sample can be rotated with the rotation axis being parallel but off-set from the optical axis [9]. This leads to a distribution of the laser power over a larger excited

area and thus reduces the heating effect. The cell construction, however, becomes relatively complex. The same effect can be achieved, when the laser beam is guided along a circular trace over the surface of the sample in a fixed position. This can be done by rotating the focusing lens around the optical axis with the lens axis being parallel to but off-set from the optical axis. This rotating lens system was first described by Zimmerer and Kiefer [10] and applied for catalytic in situ Raman studies by Synder and Hill [11].

5. The most critical problem with LRS is probably the possible appearance of an intense background, usually called fluorescence. This can be caused by sample impurities or contaminations, but also by surface hydroxyl groups [12], by the sample itself or by adsorbates on its surface. The experimentalist can cope with the fluorescence in various ways. One can in principle avoid exciting the fluorescence by using another excitation wavelength. FT-Raman spectroscopy provides the possibility of IR-excitation with a Nd:YAG laser ($\lambda_{exc} = 1.064$ μm) and data acquisition with an FTIR-spectrometer, but it has the disadvantage of the low excitation frequency. The Raman intensity is proportional to ν_{exc}^4.

Time-resolved techniques can be used to overcome fluorescence problems. However, they are very complex and will hardly be applied as routine techniques for catalytic studies.

In contrast, frequency modulation techniques [13] can successfully be applied to remove fluorescence backgrounds and can be relatively easily implemented in a commercial laser-spectrometer system [14].

Perhaps the simplest procedure to remove the fluorescence background from raw spectra is the background subtraction, although this can lead to artefacts and spurious bands, particularly when optical multichannel detectors are being used. This unfavourable situation can be significantly improved by the application of the scanning multichannel technique (SMT) [15,16].

3. Raman studies of molybdate and VPO catalysts

Bismuth molybdate phases, such as α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, γ-Bi_2MoO_6, are important components in BiMo-oxide catalysts which have high activities for partial oxidation and ammoxidation of alkenes [17,18]. Since the application of Raman spectroscopy for studies of these catalyst systems has been reviewed [2], this subject will only be covered very briefly here particularly mentioning those investigations which have been carried out under in situ conditions.

Many of the reported Raman studies involve the identification of the different bismuth molybdate phases. This is not an easy task since catalytic materials are typically multiphasic and the lattices of individual phases are highly distorted so that a clear distinction between octahedral and tetrahedral coordinations is often difficult. The most thorough early vibrational analysis was reported by Matsuura et al. [19]. Hardcastle and Wachs [4,20] have recently reported direct relationships between metal–oxygen Raman stretching frequencies and bond strength (bond length) using the diatomic oscillator approximation. Snyder and Hill [11] investigated the partial oxidation of propene under reaction conditions by LRS. Their in situ studies demonstrated that α-, β- and γ-bismuth molybdate phases were completely stable under typical partial oxidation conditions.

Several Raman studies of sites responsible for activity and/or selectivity have used isotope labelling by ^{18}O. The work of Keulks and coworkers [21,22] was the first non-in situ Raman investigation that demonstrated the active participation of lattice oxygen in partial oxidation and its incorporation into the reaction products. Ono and Ogata [23] recently determined the location of ^{18}O tracers in the lattices of γ-Bi_2MoO_6 and α-$Bi_2Mo_3O_{12}$ after exchange. With the γ-phase, all types of lattice oxygens could be exchanged with gas phase $^{18}O_2$, while with the α-phase, the lattice oxygens that exchanged were those of

Mo tetrahedra with adjacent Bi ions. Oxygens situated next to Bi ion vacancies did not exchange initially. In the catalytic oxidation of propene on the α-phase, oxygen uptake also occurred at the terminal oxygen vacancies.

The first in situ LRS study under selective alkene oxidation conditions which achieved direct structural identification of catalytically active oxide ions was reported by Glaeser et al. [24]. The spectroscopic examination of bismuth molybdate reduced with selected probe molecules such as but-1-ene, propene, methanol and ammonia, when reoxidized with $^{18}O_2$, established the existence of the multifunctional nature of active sites for propene oxidation and ammoxidation. α-H abstraction occurs by oxide ions bridging bismuth and molybdenum atoms, and the oxygen or NH group inserted into the allylic intermediate originates from bridging centres between molybdenum atoms. The directed lone pairs of electrons associated with Bi-O-Bi species in the multifunctional site are responsible for dioxygen chemisorption, reduction and dissociation.

An analogous LRS study was performed by Schrader et al. [25,26] on VPO catalysts which are active for *n*-butane oxidation. Two types of sites I and II were identified which were primarily responsible for complete combustion or for selective oxidation, respectively. Volta and coworkers [27–31] studied the behavior of VPO catalysts during *n*-butane oxidation. These authors demonstrated that the basic phase $(VO)_2P_2O_7$ was stable under working conditions while the δ-$VOPO_4$ phase transformed into α_{II}-$VOPO_4$ [27]. The precursor $VO(HPO_4) \cdot 0.5H_2O$ became totally disordered during catalyst activation in an *n*-butane/air atmosphere with the simultaneous onset of the generation of maleic anhydride [30]. The authors concluded that the creation of the active surface may not solely depend on the nature of the bulk catalyst phase. The active sites were considered to be specifically formed under reaction conditions and requires the presence of the reacting molecules and products that may provide a template to enable surface structures of the catalyst to crystallize. In a further study, Volta and coworkers [29] investigated the role of Fe and Co promoters during the activation of the $VO(HPO_4) \cdot 0.5H_2O$ precursor of the VPO catalyst by in situ Raman spectroscopy.

Further details of in situ LRS investigations of *n*-butane oxidation on VPO catalysts are reported by Volta et al. [27] and by Wachs [30] in this issue.

Methanol oxidation on supported molybdenum oxide catalysts was studied by in situ LRS by Hu and Wachs [31].

4. Investigations of synergy effects by in situ LRS

Ozkan et al. [32] provided evidence for catalytic synergy in partial oxidation of C_4 hydrocarbons to maleic anhydride using in situ LRS and ^{18}O isotope labelling, when simple molybdates such as $MnMoO_4$ or $CdMoO_4$ were in close contact with MoO_3. The authors suggested a 'catalytic job distribution of the two phases', in which the MoO_3 phase incorporates its lattice oxygen into the hydrocarbon molecule, while the simple molybdate phase provides the oxygen necessary to regenerate MoO_3 sites through an oxygen spillover process. In the remote control mechanism, spillover oxygen is assumed to migrate from one oxide phase (the donor) onto the surface of a second oxide phase (the acceptor), where it creates (or regenerates) active sites able to produce the selective oxidation products [33,34]. In mixtures of antimony oxides with MoO_3, the antimony oxide is considered to be the donor phase.

In an attempt to study the synergy effect between antimony oxides and MoO_3, Mestl et al. investigated the interaction with $^{18}O_2$ of the individual binary oxides Sb_2O_3, Sb_2O_4 [35] and MoO_3 [36] and of physical mixtures of the antimony oxides and MoO_3 [37] using in situ LRS. The experiments clearly demonstrated that no detectable oxygen exchange occurred between $^{18}O_2$ in the gas phase and stoichiometric binary oxides Sb_2O_4 [35] and MoO_3 [36] in the investigated temperature range up to 750 K. When Sb_2O_3 was oxidized in $^{18}O_2$, the formation of $Sb_2^{16}O_3^{18}O_x$ ($x \leq 1$) with ^{18}O incorporation was observed [35]. Reexchange with $^{16}O_2$, however, was not possible. It must therefore be concluded that ^{18}O incorporation into the lattices of the stoichiometric binary oxides is not possible unless oxygen vacancies are present. This conclusion found strong support when vacancies were created in MoO_3 by vacuum treatment at elevated temperatures which could subsequently be replenished by exposure of the MoO_{3-x} to an $^{18}O_2$ atmosphere [36].

Fig. 1a shows the Raman spectrum of MoO_3. A vibrational analysis of the MoO_3 spectrum has been reported by Py et al. [38]. For simplicity, only the three high-frequency bands at 993, 816 and 663 cm^{-1} will be considered here. A more detailed discussion of the spectrum in relation to the MoO_3 structure was given earlier [36,37]. The bands at 993 cm^{-1} and at 816 cm^{-1} correspond to Mo–O stretching modes along the crystallographic *b* and *a* axis, respectively. The band at 663 cm^{-1} represents the antisymmetric stretching mode of Mo–O–Mo bridges along the *c* axis. When this MoO_3 was treated at 648 K in vacuum (10^{-1} Pa) for 10 h, the spectrum of Fig. 1b was observed. The poorer quality of this spectrum as compared to that shown in Fig. 1a is due to the slightly bluish color of the produced MoO_{3-x} which results in an increased absorption coefficient.

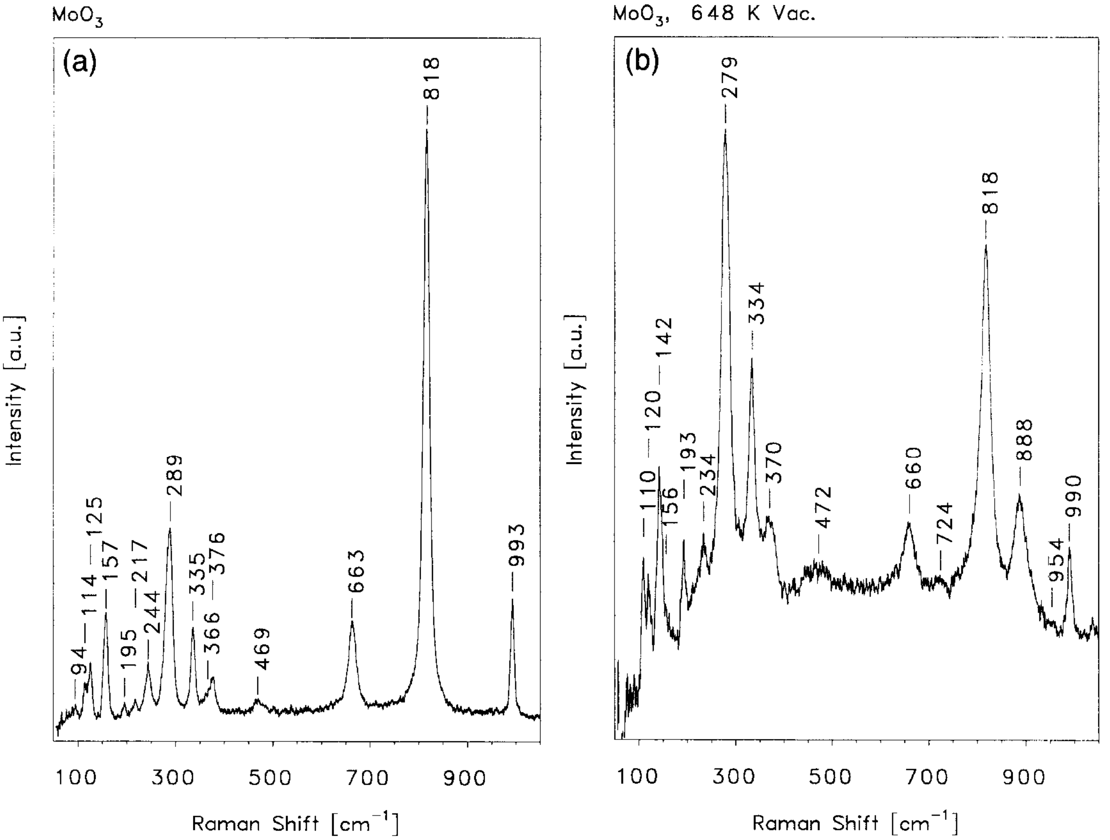

Fig. 1. (a) Room-temperature Raman spectrum of MoO_3 prior to thermal treatment. (b) In situ high-temperature Raman spectrum of MoO_{3-x} after evacuation to 10^{-1} Pa at 648 K for 10 h (spectrum recorded at 648 K).

The relatively greater decrease of the intensity of the bands at 660 and 818 cm^{-1} as compared to that of the band at 990 cm^{-1}, suggests that oxygen atoms are more easily lost from bridging positions and from Mo–O groups oriented along the *a* axis than from Mo = O groups oriented along the *b* axis, the latter having the highest Mo–O bond order. The new band at 888 cm^{-1} and the two weak features at 724 and 954 cm^{-1} were related to the formation of shear defects in MoO_{3-x} [36]. When this material was reoxidized in an $^{18}O_2$ atmosphere, the defect bands disappeared and new bands formed at 648, 793 and 948 cm^{-1} (not shown) which could clearly be identified as Mo–^{18}O–Mo and Mo = ^{18}O vibrations. Hence, the oxygen-deficient MoO_{3-x} could be reoxidized with ^{18}O incorporation by replenishing the oxygen vacancies. Since reexchange of the resulting $Mo^{16}O^{18}_{3-x}O_x$ in an $^{16}O_2$ atmosphere was not possible, these experiments proved that oxygen-vacancies are required for incorporation of ^{18}O-labels and that simple oxygen exchange does not occur at a detectable level under the experimental conditions applied.

Fig. 2 shows the Raman spectrum that was recorded of a physical mixture of Sb_2O_3 and MoO_3 after vacuum treatment for 10 h at 648 K [37]. The intensity of the defect band of MoO_{3-x} at 883 cm^{-1} in this spectrum is relatively much higher than the corresponding band in the spectrum of pure MoO_{3-x} (Fig. 1b) and has reached the intensity of the band at 823 cm^{-1}. It was therefore concluded that the close contact with Sb_2O_3 led to enhanced reduction of MoO_3 via reverse oxygen spillover. In fact, detailed analysis of the low-frequency region of the spectrum of Fig. 2 shows that Sb_2O_3 was transformed into Sb_2O_{4-x} [37].

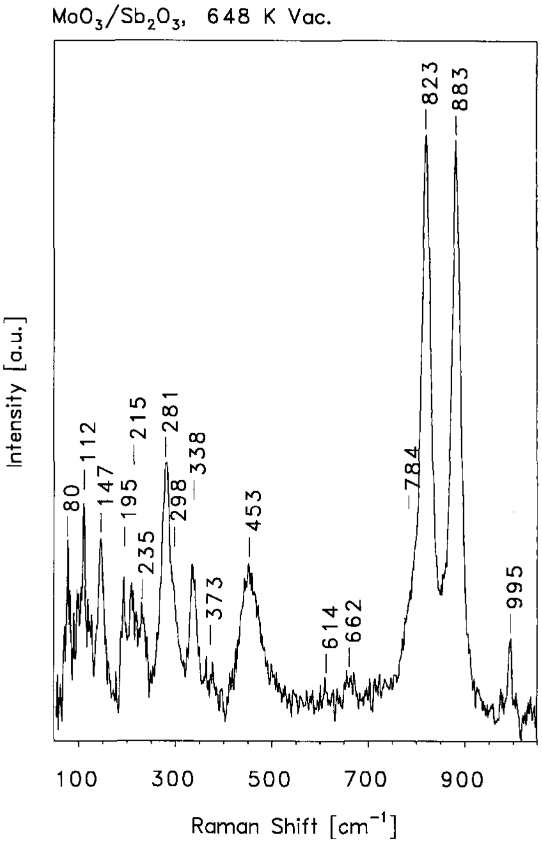

Fig. 2. High-temperature in situ-Raman spectrum (recorded at 648 K) of Sb_2O_3 /MoO_3 mixture after 10 h evacuation to 10^{-1} Pa at 648 K.

Reoxidation of this physical mixture containing oxygen-deficient Sb_2O_4 and MoO_3 phases in an $^{18}O_2$ atmosphere resulted in the spectrum shown in Fig. 3 [37]. Clearly the defect bands of MoO_{3-x} have disappeared and ^{18}O incorporation into the MoO_3 lattice is indicated by the appearance of the Mo = ^{18}O bands at 793 and 945 cm^{-1}. The strong band at 191 cm^{-1} is due to the formation Sb_2O_4. Reexchange with $^{16}O_2$ was not possible consistent with the fact that ^{18}O incorporation was not observed in mixtures of Sb_2O_4 and MoO_3.

The conclusions to be drawn from these experiments [37] can be summarized as follows:

1. Oxygen incorporation into the oxide lattices of antimony and molybdenum oxides as individual oxides or in physical mixtures requires oxygen vacancies.
2. Exchange via bulk diffusion in oxide mixtures is excluded under the applied experimental conditions.
3. Spillover oxygen, if present, remains below the detection limit.

5. High temperature in situ Raman spectroscopy of working oxidative coupling catalysts

In oxidative coupling CH_4, along with an oxidant such as O_2 or N_2O is passed over a basic catalyst at elevated temperatures to form C_2 products [39,40]. Among the various forms of surface oxygen that have been proposed to be responsible for the activation of CH_4, also the peroxide ion was discussed. For example, Na_2O_2 and BaO_2 react with CH_4 even at 670 K, to give C_2 products, although not in a catalytic cycle [41,42]. More recently, Dissanayake et al. [43] using XPS demonstrated that there was a good correlation between the intrinsic catalytic activity and the near-surface concentration of O_2^{2-} ions for a series of Ba/MgO catalysts (Ba loadings between 0.2 and 25 mol%). Peroxide ions have also been detected under reaction conditions at temperatures up to 1070 K by in situ LRS on these materials [6]. The O–O stretching band intensities (bands between 820 and 850 cm^{-1}) responded to changes in the gas phase compositions in a manner that was consistent with their involvement in the catalytic activation of CH_4.

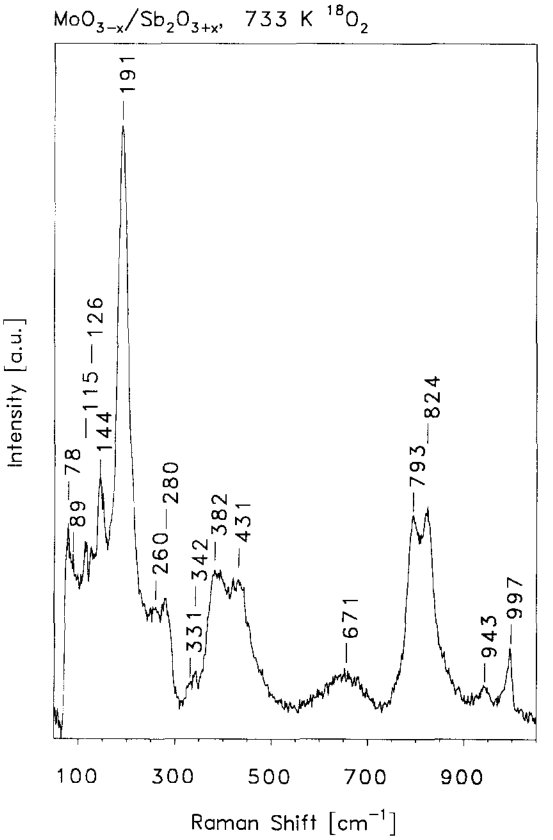

Fig. 3. High-temperature in situ-Raman spectrum (recorded at 733 K) of Sb_2O_3/MoO_3 mixture after 14 h thermal treatment at 733 K in $^{18}O_2$.

The existence of O_2^{2-} ions has also been demonstrated on La_2O_3 and Na-modified La_2O_3 [44]. As shown in Fig. 4a (spectrum a) peroxide ions (band at 863 cm^{-1}) were formed on La_2O_3 at 970 K in flowing O_2. On exposure to a He/CH_4 flow, the band was reduced in intensity, shifted to lower wavenumbers and ultimately disappeared after 80 s. The peroxide ions were restored on switching from the He/CH_4 (2:1) flow to a flow containing oxygen, namely $He/CH_4/O_2$ (8:4:1) as shown in Fig. 4b. The behaviour of the Na^+/La_2O_3 catalysts was qualitatively similar.

In summary, peroxide ions were identified by in situ LRS at high temperatures on working La_2O_3 and Na^+/La_2O_3 catalysts. The peroxide ions reacted with CH_4 in a manner consistent with their role in a catalytic cycle, and they were detectable during the actual catalytic reaction at 970 K [44]. Peroxide ions were also detected on Ba/MgO at temperatures up to 1070 K [6].

6. Methanol oxidation on Ag single crystal surfaces

Silver is widely used as a catalyst for the partial oxidation of methanol to formaldehyde at temperatures of about 1200 K. Using a specialized in situ cell combined with an elliptic mirror with high collection efficiency [45], Bao et al. [46,47] carried out model studies by in situ LRS on Ag(111) and (110) single crystal surfaces. The Ag surface was restructured during high-temperature oxygen treatment causing micro facets with dimensions in the range 0.5 to 1 μm

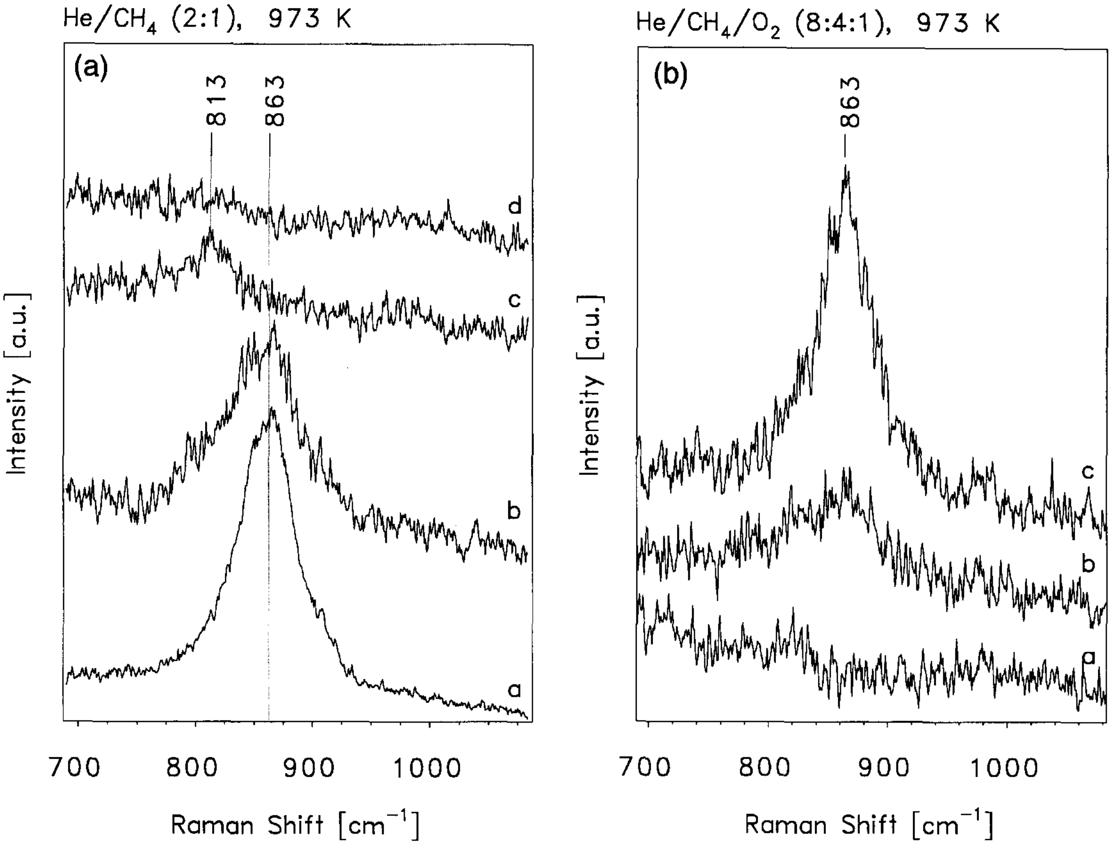

Fig. 4. (a)Time-resolved in situ high-temperature Raman spectra of La_2O_3 in contact with a He/CH_4 (2:1) mixture at 970 K: (a) spectrum obtained after activation in O_2 at 970 K for 16 h; (b) spectrum recorded 16 s; (c) 32 s; and (d) 80 s after CH_4 entered the in situ cell. (b) Time-resolved in situ high-temperature Raman spectra of La_2O_3 during treatment of the catalyst at 970 K in a $He/CH_4/O_2$ (8:4:1) mixture: (a) prior to exposure to the O_2-containing mixture; (b) 64 s; and (c) 224 s after the mixture entered the in situ cell.

favourable for strong surface enhancement by a factor $> 10^3$. The enhancement was shown to be produced by a cooperation of both the delocalized electromagnetic and the localized charge transfer mechanism [48]. Three Ag–O vibration modes were detected at 954, 630 and 803 cm^{-1} which were denoted α-, β- and γ-species, respectively. The α-species is weakly bound and only present at temperatures ≤ 600 K but not under catalytic conditions. The O_β and O_γ species could be produced by exposure of the Ag crystal in an O_2 atmosphere. Applying additional surface analysis techniques, it could be shown that O_β was a bulk species while O_γ was a strongly bonded surface oxygen species which existed at temperatures up to 1170 K [46]. When a fully oxygen-saturated surface was exposed to methanol vapour in the presence of O_2 at 850 K, the O_γ-species reacted with the methanol suggesting that this species was involved in the methanol reaction to formaldehyde [46]. It was also demonstrated that an equilibrium was established between the bulk O_β- and the surface O_γ-species.

In conclusion, in situ model LRS studies can be carried out even using Ag single crystal surfaces, which identified three different oxygen species. The O_γ-species were shown to be oxygen atoms on the surface of the distorted Ag lattice. The O_γ-species was involved in the oxidation of methanol to formaldehyde. It was also shown by in situ LRS that the O_γ-species were promoted by H_2O via surface OH species [48].

7. Conclusions

LRS is an ideally suitable technique for in situ investigations under extreme temperature (and pressure) conditions. LRS studies of working oxidation catalysts provide information on structures and structural transformation of the solid catalysts under reaction conditions. Oxygen labelling experiments permit studies of exchange properties and of reduction/reoxidation processes. Information on the nature of adsorbates being present under working conditions including possible catalytic intermediates may be obtained, and hence, well-designed experiments may provide information of high significance for elucidation of catalytic mechanisms.

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