Photooxidation

Laser-Induced Formation of Metal–Peroxide Linkages on the Surface of Lanthanum Sesquioxide under Oxygen**

Wei Zheng Weng, Hui Lin Wan,* Jian Mei Li, and Ze Xing Cao*

Dedicated to Professor Khi Rui Tsai on the occasion of his 90th birthday

Laser Raman spectroscopy (LRS) is extensively used for analyzing molecular vibrational spectra, generally as a complimentary technique to IR spectroscopy, and specifically for in situ applications owing to its simplicity and maneuverability. In particular, LRS has been widely used for in situ examination of surface structures and reaction intermediates in metal oxide catalysts under working conditions.[1] When studying lanthanide oxide based catalysts for selective oxidation of methane or ethane by in situ LRS, measurements must be carried out at an elevated temperature in the presence of oxygen to simulate the catalytic conditions and provide information on, amongst others, active oxygen species.[2] Recently, during a study on La_2O_3-based catalysts by microprobe LRS, we discovered that the laser not only acted as an excitation source for Raman scattering but also induced the formation of a metal peroxide on the La_2O_3 surface. The implications of the observation are far reaching, since they indicate that LRS results may be complicated by an artifact arising from laser excitation. This also raises questions about the photophysics and photochemistry of La_2O_3 surfaces and their relation to catalytic activity. We took advantage of the ready-made configuration and energy-delivery and detection systems of microprobe LRS to study surface photooxygenation of some lanthanide sesquioxides and thier subsequent reaction with ethane. We demonstrate that a lanthanum peroxide linkage is formed by irradiating La_2O_3 with a laser under oxygen and reacts with ethane in a catalytic fashion. The results reported below were obtained in an in situ Raman cell designed for microprobe LRS under standard conditions (under flowing oxygen, 514.5 nm excitation laser at 5 mW, 400 °C) unless otherwise specified. Further experimental details are given in the Supporting Information.

La_2O_3 is characterized by three Raman bands in the regions 406–397, 190–184, and 104–101 cm^{-1} arising from the stretching and bending of La–O^{II} bonds;[3] elevated temperatures (e.g., 400 °C) may cause shifts to lower frequencies. On irradiation of La_2O_3 in the in situ Raman cell with a continuous-wave excitation laser (514.5 nm) at 400 °C under oxygen, a new set of bands at 835–841, 289, and 240 cm^{-1} start to emerge at the expense of the $\nu_{La-O^{II}}$ stretching band at 397 cm^{-1} (Figure 1). These concurrent changes induced by laser irradiation became noticeable after several minutes and displayed well-defined isosbestic points at 558 and 389 cm^{-1}. Comparable changes in LRS bands were also recorded for other Ln_2O_3 samples under O_2 at elevated temperatures; for example, the stretching band of Nd_2O_3 at 434 cm^{-1} was replaced by a band at 849 cm^{-1}, and that of Sm_2O_3 at 331 cm^{-1} by one at 836 cm^{-1}, on laser irradiation (Supporting Information). As such changes did not occur under nitrogen, the new Raman bands must arise from photooxygenation of the La_2O_3 surface to a lanthanum peroxide. The major band at $\approx$840 cm^{-1} can be assigned to the O_2^{2-} stretching mode, and the other two minor bands to the La^{3+}–O_2^{2-} bending mode, by comparison with the assignment for neodymium(III) oxide peroxide $[Nd_2O_2(O_2)]$.[4] The spectrum of photooxygenated La_2O_3 (Supporting Information) is comparable to, but shifted from, that of $[Nd_2O_2(O_2)]$ prepared from Nd_2O_3 and KO_2 at 1500 °C and 40 kbar.[4] In contrast to such extreme conditions, the present peroxide is formed by mild photooxidation, where laser excitation provides the necessary energy to power the unique surface reaction transforming La–O^{II} into La^{3+}–O_2^{2-} under oxygen, as cogently demonstrated by the exact

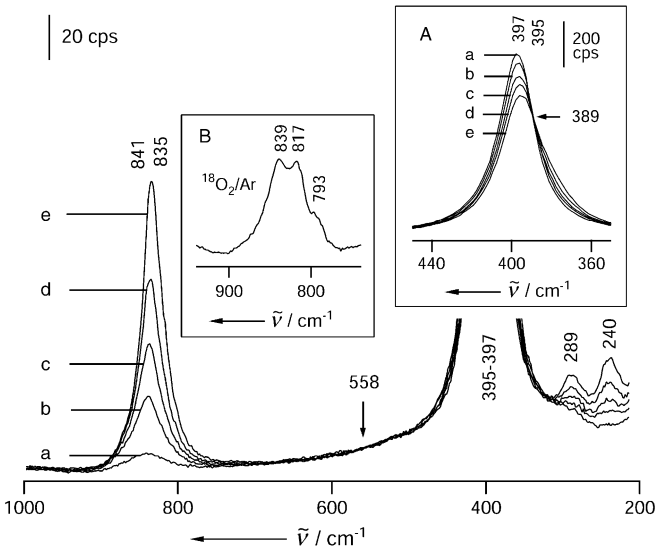

Figure 1. In situ Raman spectra of La_2O_3 continuously irradiated with a focused laser beam (514.5 nm, 5 mW) under $^{16}O_2$ in a microprobe Raman spectrometer at 400 °C for 1, 4, 9, 18, and 60 min (a–e). Inset A: the $\nu_{La-O^{II}}$ peak recorded under $^{16}O_2$ atmosphere. Inset B: the pattern of ν_{O-O} isotopic peaks recorded for the ^{18}O-labeled sample at room temperature.

[*] Prof. Dr. W. Z. Weng, Prof. Dr. H. L. Wan, J. M. Li, Prof. Dr. Z. X. Cao
State Key Laboratory for Physical Chemistry of Solid Surfaces
Department of Chemistry, Institute of Physical Chemistry
Xiamen University, Xiamen, 361005 (China)
Fax: (+86) 592-218-1395
E-mail: wzweng@xmu.edu.cn
hlwan@xum.edu.cn

[**] Supported by the Ministry of Science and Technology of China (G1999022408) and the National Natural Science Foundation of China (20021002 and 20233020). We thank Prof. Yuan L. Chow for stimulating discussions and revision of the manuscript, Prof. Yuan Yan Liao for designing and manufacturing the in situ Raman cell, and Prof. Chuan Jing Huang and Guo Kun Liu for their help in the experiments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

 DOI: 10.1002/ange.200351706

isosbestic points in Figure 1. Formation of a peroxide linkage with a band at $\approx 840\ cm^{-1}$ was further confirmed by using 3% $^{18}O_2$ in Ar to perform the laser-induced photooxygenation. Figure 1B shows side peaks at 817 and 793 cm^{-1} corresponding to isotopic peroxide linkages $[^{16}O^{18}O]^{2-}$ and $^{18}O_2^{2-}$, respectively, perched on the slope of the main peak at 839 cm^{-1} (for $^{16}O_2^{2-}$).

The requirement for laser excitation was further demonstrated by three experiments. On irradiating La_2O_3 under oxygen at 400°C with a 514.5 nm laser, the 837 cm^{-1} band increased in intensity in proportion to the irradiation time, remained static when the laser was switched off, and increased again when the laser was switched back on (Figure 2a).

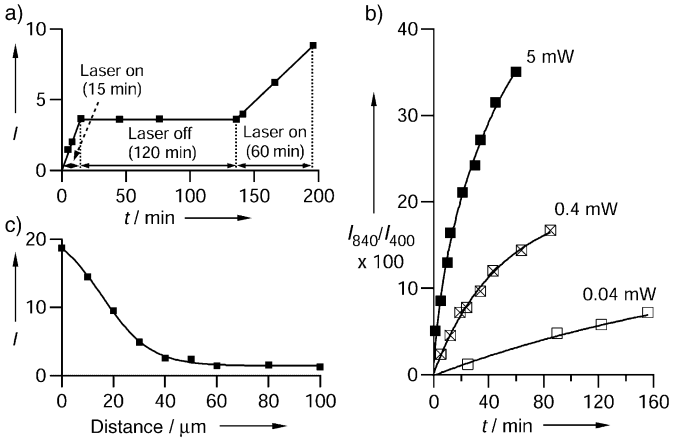

Figure 2. Effects of 514.5 nm laser irradiation (at 5 mW and 400°C unless otherwise specified) on the formation of peroxide species over La_2O_3 under O_2. a) Response of 837 cm^{-1} peak intensity to the duration of laser action. b) Intensity ratio of the peaks at ≈ 840 and $\approx 400\ cm^{-1}$ (I_{840}/I_{400}) as a function of time with laser powers of 5, 0.4, and 0.04 mW. c) Plot of 837 cm^{-1} peak intensity against the distance from the center of the laser beam (≈ 4 μm in diameter) after irradiation at 400°C for 130 min followed by at 300°C for a further 85 min.

Figure 2b shows the response of the same band as a function of the applied laser power under similar conditions. Finally, Figure 2c plots the intensity of the same 837 cm^{-1} band against the distance from the center of the laser beam (≈ 4 μm in diameter); the intensity attenuated with increasing distance from the center, and became almost zero at 40–50 μm. The pattern indicated that laser irradiation but not thermal heating causes the formation of La–peroxide linkages, although so far the latter interpretation has been generally considered to be correct.[2a,5]

Whereas extended heating of La_2O_3 at high temperature (>650°C) resulted in insignificant intensity at 840 cm^{-1}, the formation and decay of this peroxide band was closely related to laser energy output in conjunction with operating temperatures. In microprobe LRS measurements under oxygen with laser excitation at 514.5 nm (55.6 kcal mol^{-1}) for a fixed time, the 840 cm^{-1} band intensity was insignificant at 100°C, but increased slowly from 200°C and peaked at about 450°C, above which the intensity started to decrease and became weak at about 600°C (see Figure 3a). Under comparable conditions, laser excitation at 632.8 nm (45.2 kcal mol^{-1})

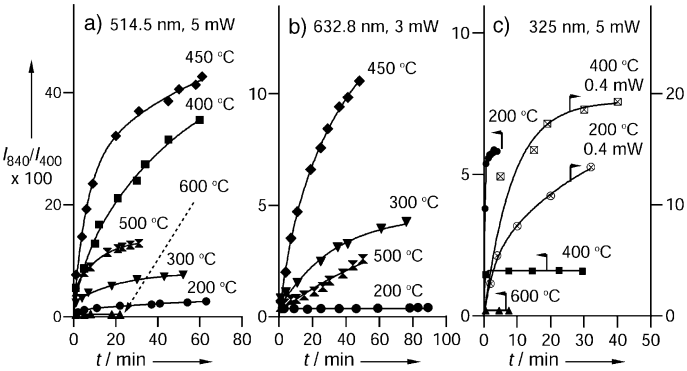

Figure 3. Plots of I_{840}/I_{400} as a function of time for continuous irradiation of La_2O_3 under O_2 with lasers at the indicated temperatures: a) 514.5 nm, 5 mW; b) 632.8 nm, 3 mW; c) 325 nm, 5 mW (unless where otherwise indicated: the measurements at 0.4 mW correspond to values of I_{840}/I_{400} shown on the axis on the right-hand side).

resulted in a weaker buildup of the peroxide-band intensity (see Figure 3b), but the higher energy 325 nm (88 kcal mol^{-1}) excitation led to weak signals even at lower temperatures, clearly owing to peroxide decomposition (see Figure 3c). In contrast, laser excitation at 785 nm (36.4 kcal mol^{-1}) did not cause formation of peroxide species up to 500°C. The pattern of formation of the 840 cm^{-1} band is typical for the requirement of photoexcitation, whereby the intensity is proportional to irradiation time and power, and a certain minimum laser energy (energy threshold) is required to cause the transition.

Such transformations are intimately related to the photophysics and photochemistry of molecular oxygen, as well as to the interaction of O_2 with lanthanum oxide. Preliminary theoretical calculations with a simplified surface cluster model show that the triplet ground state of O_2 is only loosely associated with the La_2O_3 surface structure, while singlet O_2 can be dissociatively adsorbed on the La_2O_3 surface to generate peroxide species with an activation energy of about 20 kcal mol^{-1}. O_2 has two low-lying singlet excited states: $a^1\Delta_g$ (at 22.5 kcal mol^{-1}) and $b^1\Sigma_g^+$ (at 37.5 kcal mol^{-1}). Owing to the prevailing heavy-atom effects of lanthanides arising from spin–orbit coupling, as is observed in solution,[6] on excitation at the metal oxide center the loose complexes can undergo facile intersystem crossing to reach singlet oxygen in the bound state. Considering the available irradiation energy (>36.4 kcal mol^{-1}, corresponding to a 785 nm laser) and the transition probabilities from the ground state of oxygen ($^3\Sigma_g^-$) to $^1\Sigma_g^+$ and $^1\Delta_g$, singlet oxygen in the $^1\Sigma_g^+$ state (at 37.5 kcal mol^{-1}) should be more accessible than that in the $^1\Delta_g$ state, and its surface-adsorbed state can be regarded as a precursor for the formation of oxidizing species.

The requirement for photoexcitation led us to study the reactivity of the peroxide. As shown in the Supporting Information, the peroxide species generated on the La_2O_3 surface by laser excitation under oxygen and the usual conditions decomposed slowly under N_2 (spectra b, c), but was immediately consumed by ethane (spectrum d). When the gas flow was changed to a mixture of C_2H_6/O_2 (2/1), as used in the actual oxidative dehydrogenation (for 6 min),

peroxide-band intensity was regained (spectrum e) and became stronger on switching to pure oxygen again (spectrum f). Both changes in the peroxide band in spectra d and e were accompanied by growth of the band at 1071 cm^{-1} for carbonate formed by adsorption of CO_2 (a by-product of the reaction between C_2H_6 and O_2^{2-}) on La_2O_3. The pattern clearly demonstrates that the surface peroxide not only reacts with ethane but also does so in catalytic fashion in the presence of oxygen. Similar sequential spectral progressions can be recorded for Sm_2O_3 under comparable conditions (Supporting Information). However, since the total amount of peroxide generated by the laser is very limited (the focused laser spot on the sample is only a few micrometers in diameter), we are unable to analyze the other products of the reaction (e.g., C_2H_4) in the gas phase.

A peroxide has been proposed as active oxygen species in catalytic oxidation of methane and ethane to ethylene over metal (including lanthanides) oxide catalysts in thermal processes.[7] The spectral comparison described here suggests that the present peroxide should have the same type of linkage but may be located in a different environment than that generated in thermal catalytic processes. The possibility of using photoinduced surface activation of oxygen in related catalytic processes remains to be studied.

We have shown that laser excitation causes photoinduced formation of lanthanide peroxide linkages on the Ln_2O_3 surface under oxygen, and demonstrated the reactivity of the peroxide with ethane at elevated temperature. Thus, we have defined a limiting condition for LRS measurements, and established a prototype instrument for investigating photoreactions of a solid surface by LRS.

Received: April 22, 2003
Revised: November 19, 2003 [Z51706]

Keywords: lanthanides · laser chemistry · oxides · peroxides · Raman spectroscopy

[1] a) G. Mestl, H. Knözinger in *Handbook of Heterogeneous Catalysis*, *Vol. 2* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), VCH, Weinheim, **1997**, p. 539; b) H. Knözinger, *Catal. Today* **1996**, *32*, 71; c) G. Mestl, T. K. K. Srinivasan, *Catal. Rev. Sci. Eng.* **1998**, *40*, 451; d) H. Knözinger, G. Mestl, *Top. Catal.* **1999**, *8*, 45; e) I. E. Wachs, *Top. Catal.* **1999**, *8*, 57; f) G. Mestl, *J. Mol. Catal. A* **2000**, *158*, 45; g) A. Bruckner, *Catal. Rev.* **2003**, *45*, 97.

[2] a) G. Mestl, H. Knözinger, J. H. Lunsford, *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 319; b) Y. D. Liu, H. B. Zhang, G. D. Lin, Y. Y. Liao, K. R. Tsai, *J. Chem. Soc. Chem. Commun.* **1994**, 1871; c) H. B. Zhang, G. D. Lin, H. L. Wan, Y. D. Liu, W. Z. Weng, J. X. Cai, Y. F. Shen, K. R. Tsai, *Catal. Lett.* **2001**, *73*, 141.

[3] a) C. R. Gopinath, I. D. Brown, *J. Raman Spectrosc.* **1982**, *12*, 278; b) J. Gouteron, D. Michel, A. M. Lejus, J. Zarembowitch, *J. Solid State Chem.* **1981**, *38*, 288.

[4] a) A. M. Heyns, K. J. Range, *J. Raman Spectrosc.* **1994**, *25*, 855; b) K. J. Range, M. Stadler, F. Rau, U. Klement, *Angew. Chem.* **1987**, *99*, 1176; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1174.

[5] M. S. Palmer, M. Neurock, M. M. Olken, *J. Am. Chem. Soc.* **2002**, *124*, 8452.

[6] J. H. Zhou, S. Q. Xia, J. R. Chen, X. S. Wang, B. W. Zhang, *Chem. Commun.* **2003**, 1372.

[7] a) K. Otsuka, K. Jinno, *Inorg. Chim. Acta* **1986**, *121*, 237; b) K. Otsuka, A. A. Said, K. Jinno, T. Komatsu, *Chem. Lett.* **1987**, 77; c) K. C. C. Kharas, J. H. Lunsford, *J. Am. Chem. Soc.* **1989**, *111*, 2336; d) J. H. Lunsford, X. Yang, K. Haller, J. Laane, G. Mestl, H. Knözinger, *J. Phys. Chem.* **1993**, *97*, 13810; e) H. Yamashita, Y. Machida, A. Tomita, *Appl. Catal.* **1991**, *79*, 203; f) D. Dissanayake, J. H. Lunsford, M. P. Rosynek, *J. Catal.* **1993**, *143*, 286; g) H. X. Dai, C. F. Ng, C. T. Au, *Appl. Catal. A* **2000**, *202*, 1.

