

RESEARCH NOTE

Raman Spectra of La₂O₃ Dispersed on γ -Al₂O₃

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Raman spectra have been obtained for La₂O₃ dispersed on Al₂O₃, but only after La₂O₃ coverages reach one theoretical monolayer or higher. Sharp peaks at 104, 191, and 408 cm⁻¹ were observed, which are in excellent agreement with previous studies of bulk La₂O₃; however, two additional broader, but intense bands not previously reported were also observed at 322 and 935 cm⁻¹. These latter two bands disappear at temperatures of 450 K or higher, but they returned with full intensity upon cooling to 300 K. A sample of bulk La₂O₃ (a-form) with a low surface/volume ratio also exhibited weak peaks at these latter two positions. Raman spectra taken with different exciting laser lines showed that the bands at 322 and 935 cm⁻¹ can be attributed to a laser-excited luminescence. It is inferred that these luminescence bands are evidence for the presence of oxygen anion vacancies. After exposure to NO at 300 K, two peaks developed at 747 and 1047 cm⁻¹ which can be assigned to a surface nitrate species. © 1998 Academic Press

Lanthanum oxide dispersed on alumina is a system of considerable interest for at least two reasons. First, it has been stated that La₂O₃ is the best-known inhibitor of sintering in γ - and other transition aluminas (1), thus it can have a role in automotive exhaust catalysts. Second, La₂O₃ has been found to be a selective catalyst for the reduction of NO_x to N₂ with CH₄ in excess O₂ (2,3). The low surface area of La₂O₃ prohibits any commercial application; however, an obvious method to improve the catalytic activity is to disperse La₂O₃ on a high surface area oxide, such as γ -Al₂O₃, and this approach has indeed resulted in catalysts with higher activity than Co/ZSM-5 at high temperatures, i.e. around 900 K and above (4).

For example, a family of La₂O₃/ γ -Al₂O₃ catalysts was prepared by impregnating γ -Al₂O₃ (Engelhard, 170 m²/g) with a solution of lanthanum acetate (Molycorp, 99%, 14.54% in H₂O) using an incipient wetness technique involving multiple impregnations (4). As the weight loading of La₂O₃ increased from 5% to 70%, turnover frequencies

increased continuously to approach that of pure La₂O₃, whereas rates (mol/s/g cat) went through a maximum at 40 wt% (4). A comparison of rates, specific activities, and turnover frequencies is provided in Table 1. Additional information about the chemical state of the dispersed La₂O₃ and the presence of any NO_x surface species would be highly desirable, and *in situ* DRIFTS experiments are currently in progress (5). Another spectroscopic technique that could be applicable for the characterization of dispersed La₂O₃ is Raman spectroscopy; however, no spectra of supported La₂O₃ could be found in the literature and the attempt reported by Bettman *et al.* failed to acquire a spectrum (1). This was attributed to two-dimensional, submonolayer coverages of La₂O₃ on γ -Al₂O₃ that could not be observed by XRD or Raman spectroscopy.

We report here a successful effort to observe La₂O₃ dispersed on Al₂O₃ using Raman spectroscopy. The Raman spectra were recorded with the scanning multichannel technique (6) on an OMARS 89 triple-monochromator spectrometer (Dilor) equipped with a thermoelectrically cooled CCD-camera (Princeton Instruments). The 488-nm line of an Ar⁺-ion laser (Spectra Physics, Type 2020) was used for excitation. A laser power of approximately 30 mW (measured at the sample position) was applied. The focused spot size was estimated to be about 1 μ m (samples were not rotated during measurement). The collecting optics consisted of a front objective L₁ (50-mm focal length, *f*/1.8) and a lens L₂ (300-mm focal length). The principle of the scanning multichannel technique is a stepwise change (step size 10 cm⁻¹) of the monochromator position (scanning), followed by superposition of all the spectra at different positions to a complete spectrum. For the measured samples the number of different spectra was between 110 and 360 and the measurement time was usually 10 s for each spectrum. The whole integration time for one complete spectrum was about 10 to 60 min. A plasma line at 1057 cm⁻¹ was used as an internal standard to calibrate the wavelength scale (s. * in Figs. 1, 2, and 4). The spectral resolution was 5 cm⁻¹. Dehydration of the samples was carried out in an *in situ*

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TABLE 1
Catalytic Parameters for NO Reduction by CH₄ (from Ref. (4))

Catalyst	Rate ($\mu\text{mol N}_2/\text{s} \cdot \text{g}$)	Spec. activity ($\mu\text{mol N}_2/\text{s} \cdot \text{m}^2$)	TOF (s^{-1})	E _a (kcal/mole)	NO Ads @ 300 K ($\mu\text{mol NO/g}$)
La ₂ O ₃	0.89	255	0.068	23	13
20% La ₂ O ₃ / γ -Al ₂ O ₃	1.53	12.2	0.024	18	64
40% La ₂ O ₃ / γ -Al ₂ O ₃	2.91	30.9	0.049	22	60
Co/ZSM-5	1.94	9.5	0.003	23	560

Note. Rxn. Cond.: NO = 1.8%, CH₄ = 0.45%, O₂ = 1.0%, P_{Total} = 1 atm, T = 973 K, GHSV = 10⁵ h⁻¹.

cell (7) in a flow of 50 ccm/min of dry He at 973 K for 1 h.

Figure 1 shows spectra for the 20% and 40% La₂O₃/ γ -Al₂O₃ samples after being treated in dry flowing He at 973 K for 1 h. The major bands at 104, 191, and 408 cm⁻¹ are clearly evident for 40% La₂O₃/ γ -Al₂O₃ (Fig. 1a) while the 408 cm⁻¹ band can be easily seen and the 191 band is discernable for 20% La₂O₃/ γ -Al₂O₃ (Fig. 1b). These peak positions are in excellent agreement with those reported previously for La₂O₃ (8–12), as demonstrated in Fig. 2a using

a sample of unsupported La₂O₃ (Rhone-Poulenc 99.99%) after a similar pretreatment. A spectrum for γ -Al₂O₃ is also shown in Fig. 2b to indicate the absence of any significant fluorescence with this alumina. Although we were able to record spectra for these Al₂O₃-supported La₂O₃ systems while Bettman *et al.* (1) were not, our results do not contradict theirs. Their La₂O₃ loadings gave surface concentrations below 8.5 $\mu\text{mol La atoms/m}^2$, which is their calculated value for "monolayer" coverage and differs from that of 17.2 $\mu\text{mol La atoms/m}^2$ estimated by Xie *et al.* (13).

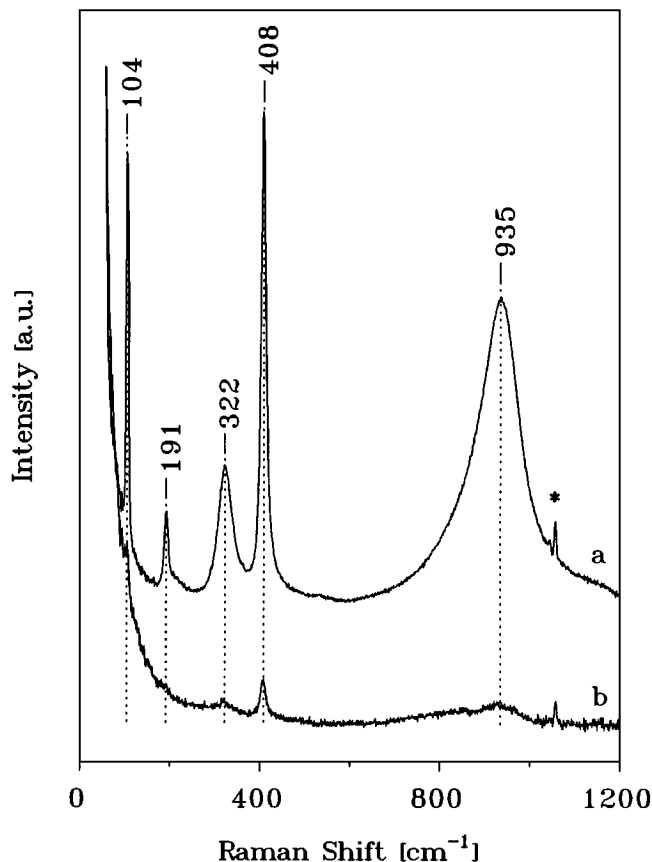


FIG. 1. Laser Raman spectra of: (a) 40% La₂O₃/ γ -Al₂O₃ and (b) 20% La₂O₃/ γ -Al₂O₃ after pretreatment in dry flowing He at 973 K for 1 h (* indicates laser plasma lines).

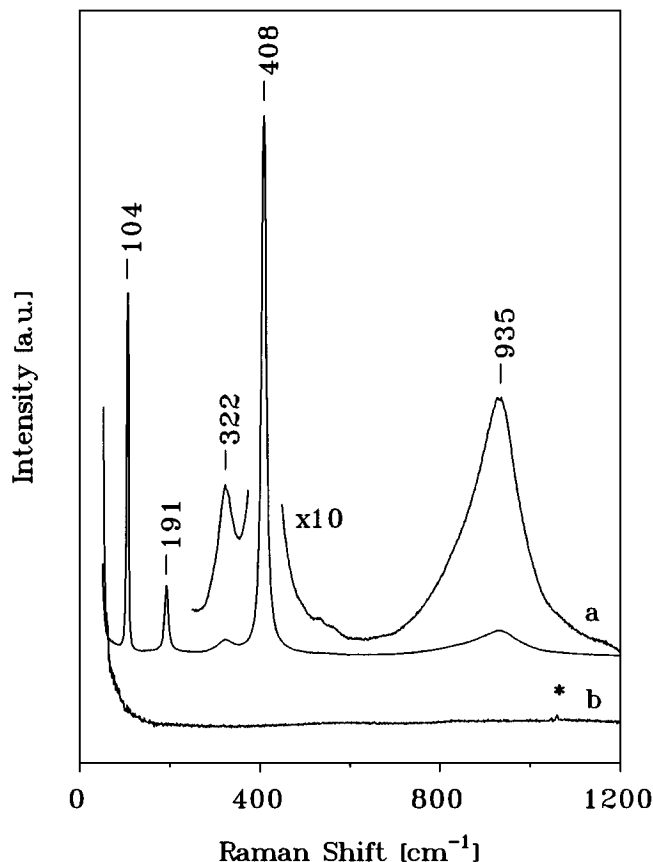


FIG. 2. Laser Raman spectra after pretreatment in dry flowing He at 973 K for 2 h: (a) unsupported La₂O₃ and (b) γ -Al₂O₃ (* indicates laser plasma lines).

Our 20% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample has a concentration of $9 \mu\text{mol La atoms/m}^2$, i.e., just over the monolayer coverage determined by Bettman *et al.* (1); the appearance of three-dimensional La_2O_3 crystallites is just detectable, as verified by X-ray diffraction (4). The 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample corresponds to 24 La atoms/m^2 and the stable, high-temperature α -form of bulk La_2O_3 is clearly evident, as verified by its XRD pattern (4). Thus these spectra strongly support the monolayer coverage of La_2O_3 on Al_2O_3 determined by Bettman *et al.* (1).

Perhaps of greater interest are the broad, very strong band near 935 cm^{-1} and the accompanying band near 322 cm^{-1} which are so obviously evident for 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (Fig. 1a), but are also observable in the 20% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (Fig. 1b) and the unsupported La_2O_3 samples (Fig. 2a). These bands have not been reported in previous studies (8–12). They do not correspond to peaks for La hydroxide or La carbonate (spectra not shown), their intensities decrease sharply as temperatures rise above 450 K so that they are essentially undetectable at 973 K, as shown by Fig. 3, yet they reform and acquire their original intensity upon cooling to 300 K. The reversibility of this temperature

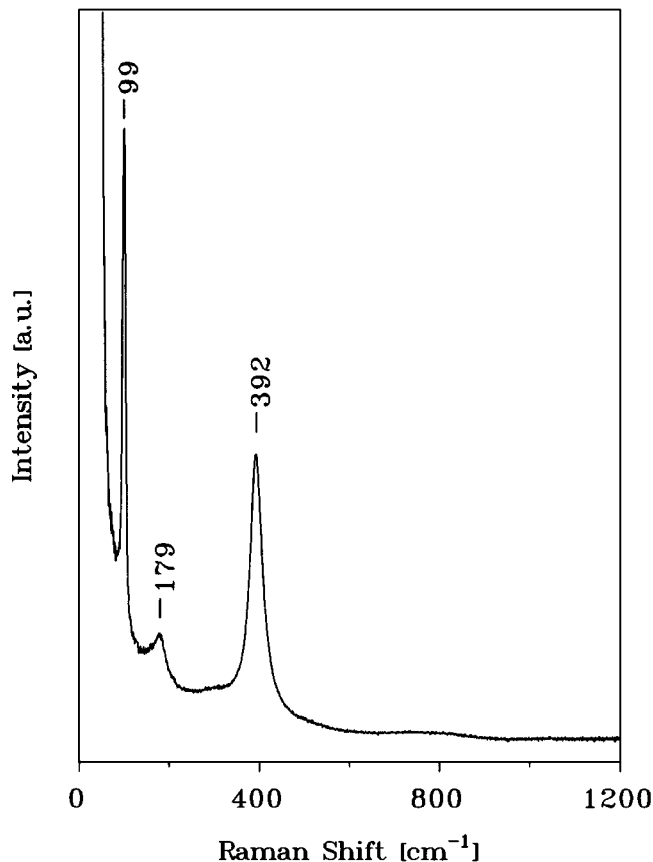


FIG. 3. High-temperature Laser Raman spectrum of 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, measured at 973 K after pretreatment in dry flowing He at 973 K for 2 h.

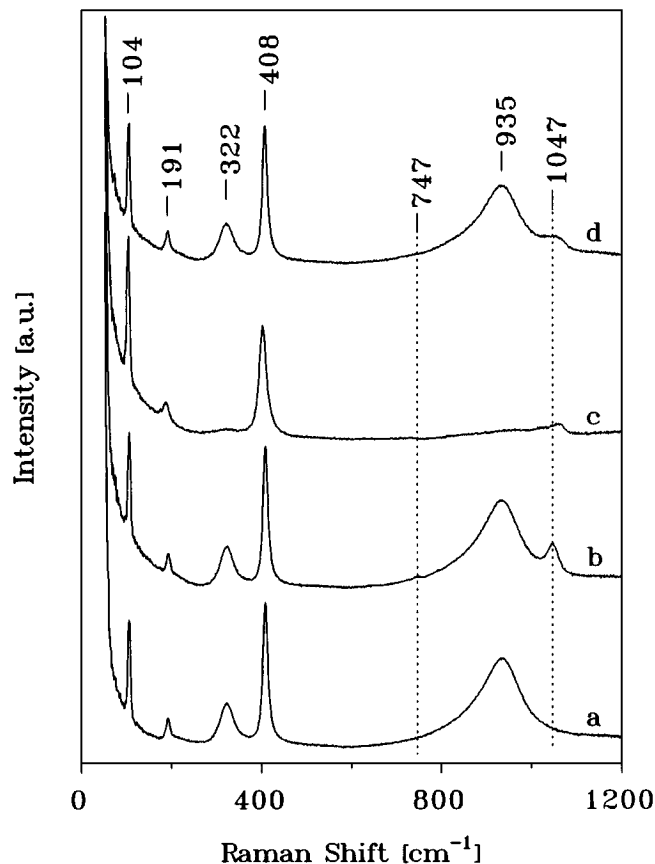


FIG. 4. Laser Raman spectra of 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ after pretreatment in dry flowing He at 973 K for 1 h, spectrum measured at: (a) 300 K; (b) after exposure to 75 Torr NO at 300 K; (c) after heating in flowing He at 448 K for 60 min (measured at 448 K); and (d) after subsequent cooling to 300 K.

effect can be clearly seen in Fig. 4. A band around 940 cm^{-1} has been observed with this La_2O_3 sample by DRIFTS after a high temperature calcination step (5,14), while the weak bands detected with the unsupported La_2O_3 are consistent with the low surface-to-volume ratio of this $3.5 \text{ m}^2/\text{g}$ sample and would argue against their assignment to $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ surface interactions.

Figure 5 shows the Raman spectra of the 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample excited with three different laser lines, namely 476.5, 488, and 514.5 nm. While the typical bands for bulk La_2O_3 at 104, 191, and 408 cm^{-1} do not shift upon changing the excitation frequency, the bands at 935 and 322 cm^{-1} (recorded at 488-nm excitation) show a different behavior which clearly depends on the excitation frequency. These spectra demonstrate that the latter two bands can be attributed to a laser-excited luminescence, but not to phonons. Raman bands will shift in absolute frequency upon changing the excitation frequency, but the shift relative to the laser frequency remains constant; however, the luminescence bands will not change their absolute frequency. The absolute position of the two shifting bands in

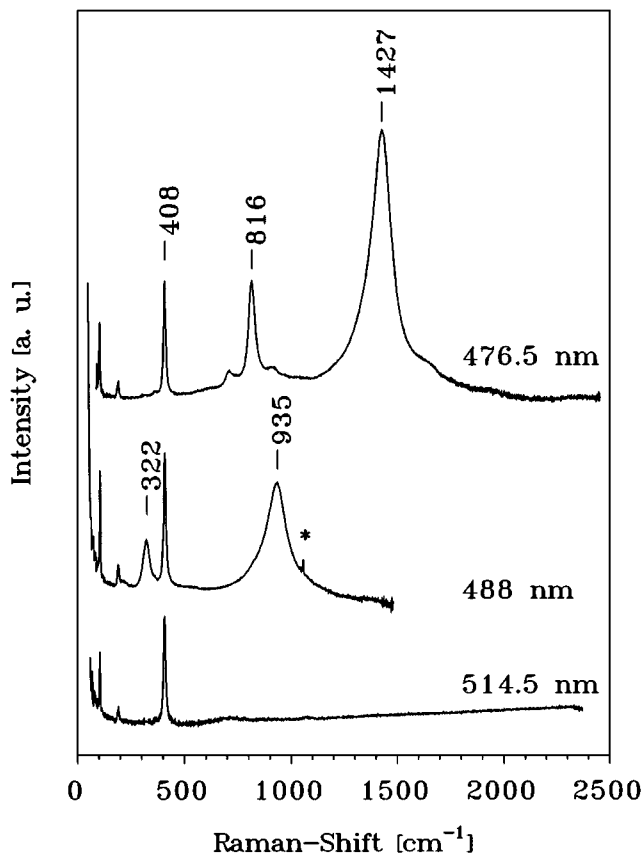


FIG. 5. Laser Raman spectra of 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ at 300 K (without pretreatment) excited with different laser lines (* indicates laser plasma lines).

Fig. 5 is 19,557 and 20,170 cm^{-1} . Moreover, not only the position, but also the intensity depends on the exciting frequency. Compared to the 488-nm line, higher intensities and additional bands were observed when using the 476.5-nm line. In the case of the 514.5-nm line, the bands would occur in the anti-Stokes regime and thus cannot be excited. An assignment of these bands to direct electronic transitions, e.g., in lanthanum atoms or cations or in impurity species, can most probably be excluded because the bands under consideration disappear completely after addition of H_2O to the sample, yielding La hydroxide (spectra not shown). After heat treatment at 973 K the bands of La_2O_3 and the luminescence bands reappear (spectra not shown).

Asher *et al.* reported similar behavior for luminescence bands in Raman spectra of zirconia (15). They observed a large number of bands with fixed absolute frequencies whose intensities changed markedly upon changing the exciting laser line. The authors divided the spectra into a series of bands of similar excitation behavior and appearance (sharp or diffuse bands). The series of sharp bands was attributed mainly to phonon-mediated recombination of excited states (exciton) of the impurity-doped zirconia. This interpretation was also given in a study of Cu_2O and its lu-

minescence spectrum (16). More interesting for the present study is the interpretation of the diffuse series in the spectra of Asher *et al.* (15). In consideration of the work by Sarver with Ti-activated zirconia (17), the authors suggested that the more diffuse luminescence bands may be associated with electron traps. It should be mentioned that the intensities of the diffuse and the dominant luminescence series in the spectra of zirconia strongly decrease with increasing temperature (18), i.e. behavior similar to that described earlier for the bands under consideration in the La_2O_3 spectrum.

Electron traps can be caused, for example, by lattice defect sites (19), and it is interesting to note that several authors have discussed the presence of oxygen anion vacancies in the La_2O_3 lattice (20–22). These unoccupied lattice oxygen sites may play an important role in both the oxidative coupling of methane and the reduction of NO_x to N_2 with CH_4 . These oxygen anion vacancies could be responsible for the transformation of adsorbed O_2 into different O-species on the surface (21), and, according to Borchert and Baerns, the mobility of the oxygen anions was dependent on the concentration of vacancies (20). It is thus inferred that the luminescence bands in the spectra of the 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample may be evidence for the presence of oxygen anion vacancies located both in the bulk and at the surface. Although little O_2 adsorption occurs on bulk La_2O_3 at 300 K (23), the stability of these sites in air at 300 K is not known because of the presence of CO_2 and water vapor. The spectra did not show significant changes prior to or after dehydroxylation at 973 K in dry He (spectra not shown). The intensity decrease of the luminescence bands with increasing temperatures may be related to the increasing mobility of the oxygen anions.

The $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts chemisorb significant amounts of NO at 300 K, as evidenced in Table 1. After the standard pretreatment in He at 973 K, exposure of 40% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ to 75 Torr NO at 300 K produced a well-defined peak at 1047 cm^{-1} and a weak peak at 747 cm^{-1} , as shown in Fig. 4, spectrum b. Heating in flowing He at 448 K for 60 min did not remove the 1047 cm^{-1} peak, as indicated by Fig. 4, spectrum c (which also clearly demonstrates the near disappearance of the 935 cm^{-1} band), although the intensity was reduced after subsequent cooling to 300 K (Fig. 5, spectrum d). The 1047 and 747 cm^{-1} peaks can be assigned to surface nitrate species based on IR spectra (14). Such surface nitrates, however, appear to be spectator species and do not seem to be involved in the catalytic cycle for NO decomposition or reduction with CH_4 (5,14,24).

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