Hydroxyl Radical Formation during the Reaction of Oxygen with Methane or Water over Basic Lanthanide Oxide Catalysts

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Abstract: Methane and molecular oxygen react over La_2O_3 and Nd_2O_3 in the temperature range 1100–1350 K to form $OH^•$ radicals which emanate into the gas phase, where they are detected using laser-induced fluorescence spectroscopy. The less basic oxides CeO_2 and Yb_2O_3 form no detectable $OH^•$ radicals. When CH_4 is replaced by a comparable amount of H_2O, the concentration of $OH^•$ radicals increases, although the apparent E_a remains constant at *ca.* 40 kcal/mol. It is concluded that the surface-catalyzed equilibrium reaction $^1/_2H_2O + ^1/_4O_2 \rightleftarrows OH^•$ is responsible for the formation of hydroxyl radicals with both CH_4 and H_2O as reagents. Consistent with the law of mass action, variation in the $OH^•$ radical concentration is 0.51 order with respect to H_2O and 0.26 order with respect to O_2. The measured concentration of $OH^•$ radicals at 1208 K with 57 mTorr of O_2 and 3 mTorr of H_2O is 1×10^{11} molecules/cm^3, which is well within experimental uncertainty of the thermodynamic equilibrium value of 4.5×10^{11} molecules/cm^3. The rotational temperature of the $OH^•$ radicals is essentially the same as the temperature of the catalyst. Hydroxyl radicals are believed to be formed by the abstraction of hydrogen atoms from H_2O, probably at surface peroxide ions. The reaction is analogous to the formation of $CH_3^•$ radicals from CH_4 on these same active oxides.

Introduction

Surface-generated gas-phase radicals may play an important role in the catalytic oxidation of hydrocarbons.[1,2] An extensively studied example is the oxidative coupling of methane, in which surface-generated $CH_3^•$ radicals couple in the gas phase to form C_2H_6 as the primary product.[3,4] Hydroxyl radicals are formed on the surfaces of various metals, such as Pt and Ni, during the oxidation of hydrocarbons, and these radicals are believed to be important intermediates in catalytic combustion.[5–8] Hydroxyl radicals are known to be chain carriers in combustion reactions. Although $OH^•$ radical formation over group VIII metals has been investigated in detail, using laser-induced fluorescence (LIF) spectroscopy, there have been no analogous studies to determine whether these radicals are formed on the strongly basic metal oxides that are active catalysts for the coupling reaction.

Certain members of the lanthanide oxide series form an interesting set for comparison of the effects of basicity and type of oxide. In the present study La_2O_3, Nd_2O_3, and Yb_2O_3 were chosen because they are sesquioxides having very different basicities, with La_2O_3 being much more basic than Yb_2O_3. In addition, CeO_2 was chosen because it is both stoichiometrically and structurally different from the sesquioxides and has multiple accessible cationic oxidation states. When compared with respect to their ability to generate C_2H_6 catalytically from CH_4 and to form $CH_3^•$ radicals, La_2O_3 and Nd_2O_3 are far superior to the other two oxides.[9–11]

Oxidative coupling reactions are usually carried out using reagent pressures between 50 and 760 Torr; however, in the present study the reagent pressures were in the mTorr range so as to minimize gas-phase reactions that could either produce or consume $OH^•$ radicals. Thus, it was possible to determine the role of the metal oxide surface as a source of $OH^•$ radicals. Under similar conditions, the formation of $CH_3^•$ radicals also was observed.

Surprisingly, the results will show that, with H_2O and O_2 as reagents, the production rate of $OH^•$ radicals is even greater than that with CH_4 and O_2 as reagents. The hydrocarbon may function only as a source of water, rather than as a source of surface $H^•$ atoms, as is believed to occur during the formation of $OH^•$ radicals on metal surfaces.[12,13] The presence of $OH^•$ radicals over the oxide surfaces is probably a result of hydrogen abstraction from H_2O, which is analogous to hydrogen abstraction from CH_4 in the formation of $CH_3^•$ radicals.

Experimental Section

Hydroxyl radicals were detected using laser-induced fluorescence (LIF) spectroscopy. The reagent gases, which included O_2 (Matheson, UHP) and either CH_4 (Matheson, UHP) or H_2O, were mixed with He (Airco, 99.95%) and introduced through a leak into a Pyrex cell with fused-silica windows. Gaseous H_2O was added by passing the total stream through a water saturator that was maintained at a known temperature. In the reactor cell, shown in Figure 1, the gases were allowed to flow over an alumina tube (4 mm o.d., 6 mm in length, Omega) that was heated internally by a platinum filament. The ends of the tube were sealed with Autostic (Carlton Brown and Assoc.) to prevent the gases from contacting the hot platinum filament. The same material was used to attach a chromel-alumel thermocouple on the external surface of the tube. The alumina tube normally was positioned parallel to and about 5 to 7 mm above the laser beam. The total pressure during most experiments was *ca.* 60 mTorr, with He diluent comprising more than 75% of the gas mixture.

The catalysts, which included La_2O_3, Nd_2O_3, Yb_2O_3, and CeO_2, were obtained from Aldrich (≥99.9% purity). A slurry, prepared by mixing the appropriate metal oxide with distilled water, was applied uniformly

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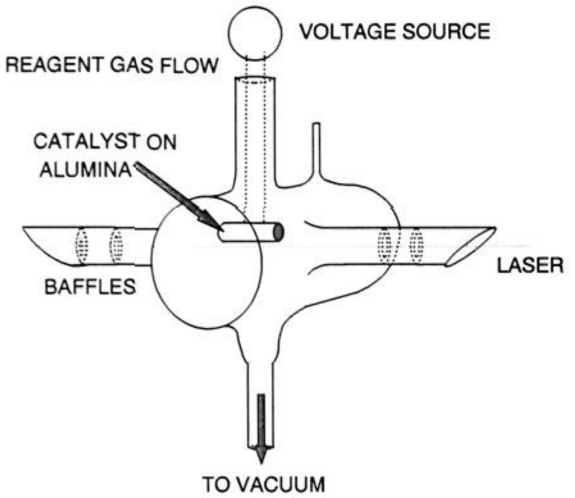

Figure 1. Schematic of the reaction cell, showing the location of the catalyst and the laser beam.

to the outside of the alumina tube. Typically, 7 mg of catalyst was added to the alumina. The catalyst and the alumina tube were then heated to 950 °C under vacuum for 8 h to convert any hydroxides or carbonates to their corresponding oxides.

The $A^2\Sigma, \nu' = 1 \leftarrow X^2\Pi, \nu = 0$ transition of the OH• radicals, which occurs at *ca.* 282 nm, was excited by the frequency-doubled output of a tunable dye laser (bandwidth ~ 0.3 cm^{-1}, pulse width = 5 ns, energy ~ 0.2 mJ/pulse). The dye laser was pumped by the second harmonic of a Q-switched Nd:YAG laser at 10 Hz. Fluorescence emission ($A^2\Sigma, \nu' = 1 \rightarrow X^2\Pi, \nu'' = 1$, near 315 nm) was collected 90° from the laser beam using two focussing lenses and was then passed through a spectrometer and measured using a UV-sensitive photomultiplier tube (PMT). Output pulses from the PMT were processed by a gated photon counter that was triggered by the Q-switch of the YAG laser. The gate width of the counter was 2 μs, which is approximately 3 times the radiative lifetime of the OH• radicals. For most of the activation energy determinations, the $Q_1(4)$ band was used because the amplitude of this band, relative to the total amplitude of all bands, varied less than 10% over the temperature range examined.

Methyl radicals were detected using a matrix-isolation electron spin resonance (MIESR) system that has been described in detail elsewhere.[2,14] The system includes a heated catalyst that is located upstream from a sapphire rod maintained at 15 K. Radicals that emanate from the catalyst bed are frozen in an argon matrix on the sapphire rod and are analyzed by ESR spectroscopy. The system was modified so that pressures in the mTorr region over the catalyst could be achieved. In one configuration, the catalyst was on the same alumina tube as used in the LIF experiments; in another configuration, the catalyst was held on a fused-quartz frit, and all of the gases flowed over the catalyst.

Results

Hydroxyl Radicals Produced during the Reaction of CH_4 with O_2. Because of our interest in the role of OH• radicals during the oxidation of CH_4 over metal oxides, CH_4 and O_2 were passed over La_2O_3, Nd_2O_3, Yb_2O_3, and CeO_2. The OH• radical spectrum observed over La_2O_3 at 1178 K is shown in Figure 2. The amplitude of the $Q_1(4)$ signal was *ca.* 30 times that of background noise. It was possible under these conditions to detect lines out to the $Q_1(9)$ transition with H_2O and O_2 as the reagents.

The production of OH• radicals as a function of temperature was determined, and the results are presented as Arrhenius plots in Figure 3. Although the number of OH• radicals generated over La_2O_3 was four times greater than that over Nd_2O_3, the apparent activation energy (see below) of ~40 kcal/mol was the same within experimental error for both catalysts. The data for each catalyst, collected over a period of 2 h during which the catalysts were stable, were obtained by randomly selecting temperatures within the range of interest. The activation energy of 40 kcal/mol was independent of the CH_4/O_2 ratio used in the experiment. Neither CeO_2 nor Yb_2O_3 gave rise to a OH• radical signal above background, with the catalysts at 1173 K.

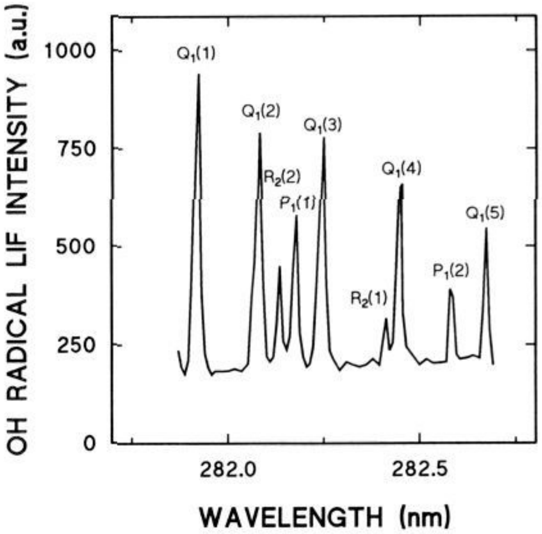

Figure 2. LIF spectrum of surface-generated gas-phase OH• radicals produced over La_2O_3 at 1178 K with 7 mTorr of CH_4 and 7 mTorr of O_2.

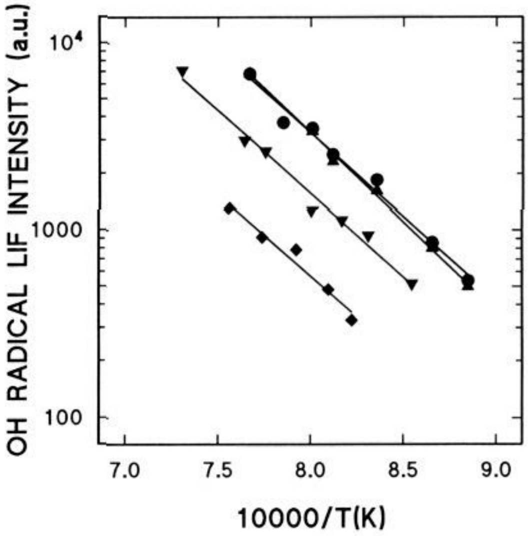

Figure 3. Arrhenius plot of OH• radical concentrations: (◆) 7 mTorr of CH_4 and 7 mTorr of O_2 over Nd_2O_3, $E_a = 40.8 \pm 3.2$ kcal/mol; (▼) 7 mTorr of CH_4 and 7 mTorr of O_2 over La_2O_3, $E_a = 39.8 \pm 1.8$ kcal/mol; (●) 7 mTorr of H_2O and 7 mTorr of O_2 over La_2O_3, $E_a = 40.8 \pm 2.0$ kcal/mol; (▲) 7 mTorr of H_2O and 7 mTorr of O_2 over Nd_2O_3, $E_a = 43.8 \pm 1.2$ kcal/mol.

To determine the effect of changing the amount of catalyst on the OH• radical production rate, the mass of La_2O_3 on the alumina tube was varied from 0 to 10 mg. As shown in Figure 4, the OH• radical concentration increased with catalyst loading, although because of the scatter in the data it is not possible to establish that the increase was linear. Nevertheless, the production rate was *approximately* proportional to the amount of catalyst, which establishes that more than the external region of the catalyst layer was involved in the generation of the observed radicals. It is significant that at 1215 K the alumina tube alone produced no radicals, confirming that the radicals are not generated thermally at the solid surface.

The relative concentrations of OH• and CH_3• radicals in the region above the surface of La_2O_3 at 1223 K are shown as a function CH_4 and O_2 pressures in Figures 5 and 6, respectively. Both radical concentrations were determined using the same

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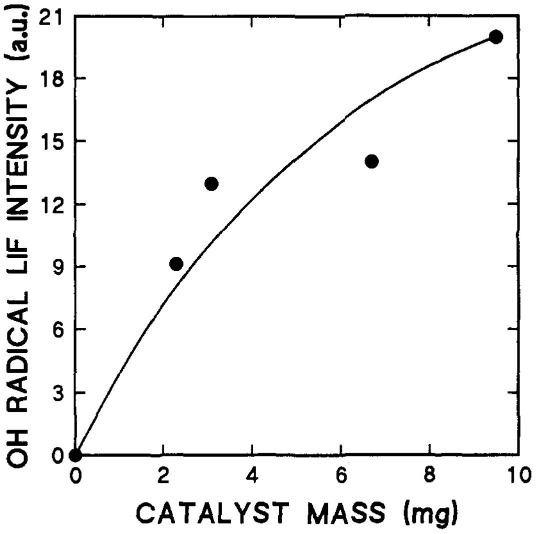

Figure 4. OH$^\bullet$ radical concentration as a function of the amount of La_2O_3 catalyst.

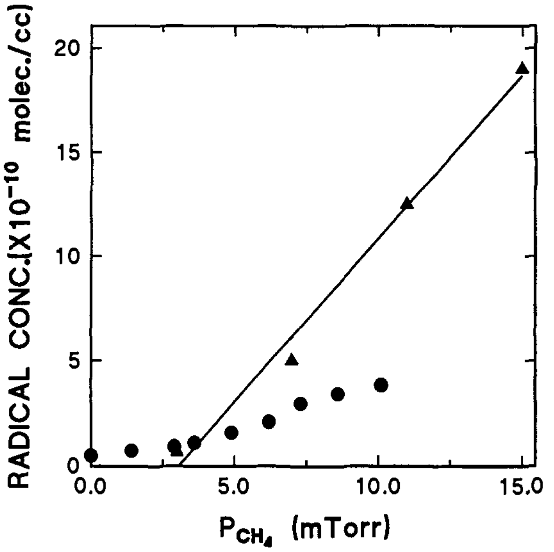

Figure 5. Effect of CH_4 partial pressure on the concentration of (●) OH$^\bullet$ radicals and (▲) $CH_3^\bullet$ radicals over La_2O_3 at 1233 K and 8 mTorr of O_2.

catalyst configuration. The OH$^\bullet$ radical concentration increased in a sigmoidal manner with respect to CH_4 partial pressure, whereas the $CH_3^\bullet$ radical concentration increased linearly. The small OH$^\bullet$ radical concentration in the absence of any CH_4 is attributed to a residual background of H_2O in the system (see below).

The functional relationships of the two types of radicals with respect to O_2 partial pressure are quite different. The OH$^\bullet$ radical concentration increased almost linearly up to *ca.* 4 mTorr of O_2, but the $CH_3^\bullet$ radical concentration decreased up to 7 mTorr of O_2. The reason for this decrease is uncertain; however, it is known that $CH_3^\bullet$ radicals are destroyed by secondary reactions with metal oxides.[11,15] Certain surface oxygen species, such as O_3^- ions, may be responsible for the destruction of $CH_3^\bullet$ radicals.[16] The same phenomenon may explain why no $CH_3^\bullet$ radicals were detected up to a CH_4/O_2 ratio of 0.3 (Figure 5). One datum point, obtained with only the alumina tube present, shows that the production of $CH_3^\bullet$ radicals also is catalytic rather than via a thermal process.

The absolute concentration of OH$^\bullet$ radicals was evaluated using the method of Schofield and Steinberg,[17] in which the intensity of the fluorescence depends on the cross section for absorption, the Einstein *A* coefficient, the quenching rates, the efficiency of the optical collection, and the volume from which fluorescence is collected. The cross section for OH$^\bullet$ radical absorption was determined by the method of McGee and McIlrath.[18] The volume and collection efficiency was determined by measuring the Rayleigh scattering of O_2 or air at a known pressure and at the same wavelength as that used for OH$^\bullet$ radical excitation. The same optics and cell were employed.

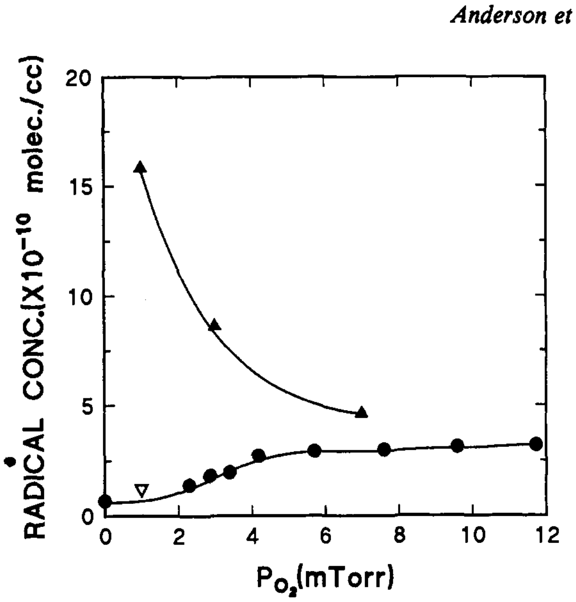

Figure 6. Effect of O_2 partial pressure on the concentration of (●) OH$^\bullet$ radicals (▲) $CH_3^\bullet$ radicals over La_2O_3 at 1233 K and 7 mTorr of CH_4. The datum point ▽ represents the $CH_3^\bullet$ radical concentration with no catalyst on the alumina tube.

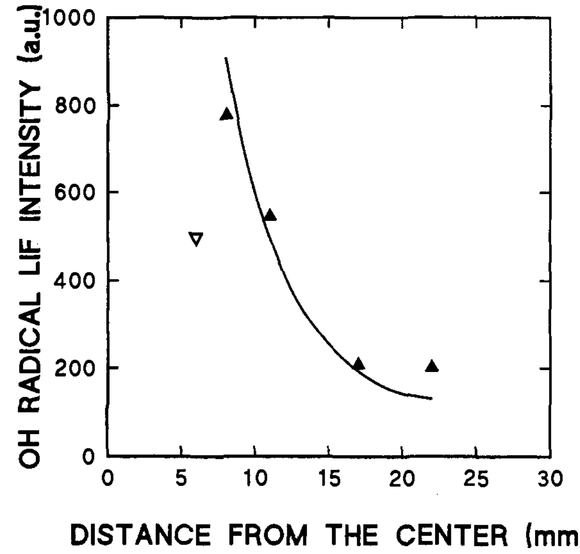

Figure 7. Variation in OH$^\bullet$ radical concentration with respect to the distance from the center of the alumina tube: (▲) the laser beam did not interact with the catalyst surface; (▽) the laser beam grazed the catalyst surface.

It was, of course, desirable to know the radical concentration just above the catalyst surface, rather than at the position of the exciting laser beam, which was typically located about 5 mm from the surface. The variation in OH$^\bullet$ radical concentration was determined with respect to the distance from the center of the alumina tube, and the results, shown in Figure 7, demonstrate that the relative radical concentration can be estimated by a $1/r^2$ dependence. This dependence becomes invalid at r values near

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5 mm, at which point the laser beam grazes the surface of the alumina tube. In this configuration, the background signal increased by a factor of more than 10, and the $OH^\bullet$ radical signal decreased. The decrease may result, in part, from scattering of light from the laser beam; however, the effect seems too large to be due primarily to scattering. In a separate study, we have found that a Raman line at 860 cm^{-1}, attributed to surface peroxide species on La_2O_3, was destroyed by 500 mW laser radiation in the visible region.[19] In the present study, the laser beam that interacts with the surface may decrease the number of centers that are responsible for generating $OH^\bullet$ radicals.

By using the $1/r^2$ dependence to extrapolate the data in Figure 7 to the surface of the catalyst, it was estimated that the concentration of $OH^\bullet$ radicals at 7 mTorr each of CH_4 and O_2 and at 1223 K was 3×10^{10} molecules/cm^3. At the same conditions, but using the MIESR flow reactor, the concentration of $CH_3^\bullet$ radicals was 5×10^{10} molecules/cm^3. The estimated error in the $CH_3^\bullet$ radical concentration is ±30%; the hydroxyl radical concentration, however, may vary by a factor of 2. It is evident, therefore, that, at least under these particular conditions, the concentrations of $OH^\bullet$ and $CH_3^\bullet$ radicals were of the same order of magnitude. The above concentrations were used to normalize the relative concentrations of the $CH_3^\bullet$ and $OH^\bullet$ radicals depicted in Figures 5 and 6.

Hydroxyl Radicals Produced in the Presence of H_2O and O_2. Even though the mean free path in the above experiments was comparable to the distance between the catalyst and the laser beam, it was necessary to confirm that appreciable concentrations of $OH^\bullet$ radicals were not formed as a result of gas-phase $CH_3^\bullet$ radical reactions, such as:

$$CH_3^\bullet + O_2 \rightarrow CH_2O + OH^\bullet \tag{1}$$

In order to demonstrate that the primary source of $OH^\bullet$ radicals was surface reactions on the catalyst, rather than gas-phase reactions, H_2O was used as a reactant instead of CH_4. Unexpectedly, at comparable reactant partial pressures, the $OH^\bullet$ radical concentration was substantially greater with H_2O as the reagent. At 7 mTorr of O_2 and 7 mTorr of either CH_4 or H_2O, the $OH^\bullet$ radical concentration over La_2O_3 was three times greater with H_2O than with CH_4.

As shown from the results in Figure 3, the apparent activation energy remained constant at ~41 kcal/mol when H_2O was substituted for CH_4 during the reaction over La_2O_3. Over Nd_2O_3, the $OH^\bullet$ radical concentration was the same as that observed with La_2O_3, but CeO_2 was again an ineffective catalyst for producing $OH^\bullet$ radicals. The common activation energy for both active catalysts, independent of reagent, and the fact that Nd_2O_3 and La_2O_3 gave the same concentration of $OH^\bullet$ radicals suggested that one might be observing the equilibrium formation of $OH^\bullet$ radicals *via* the reaction

$$\tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightleftarrows OH^\bullet \tag{2}$$

In the case of CH_4, the H_2O produced by complete oxidation of the hydrocarbon would be the source of the $OH^\bullet$ radicals.

The relevant thermodynamic functions, taken from the JANAF tables,[20] are given in Table I. At the temperatures of interest $\Delta H_r = 38.9$ kcal/mol, which is reasonably close to the value of 40–41 kcal/mol observed in this study, considering the uncertainties in our measurement and in the ΔH_f for the $OH^\bullet$ radical. In addition, the experimental (extrapolated) value for the $OH^\bullet$ radical concentration above the La_2O_3 surface is in agreement with that predicted from thermodynamic calculations (Table I). Using the $1/r^2$ fit of Figure 7 to extrapolate the concentration of $OH^\bullet$ radicals to the surface, a value of 1×10^{11} molecules/cm^3 was obtained at 1208 K, with 57 mTorr of O_2 and 3 mTorr of H_2O. The estimated thermodynamic equilibrium value is 4.5×10^{11} molecules/cm^3; however, it is obvious from Table I that even a small error in the free energy would result in a large error in the calculated concentration of $OH^\bullet$ radicals. The 5-fold difference in concentrations is well within the expected uncertainties.

Table I. Thermodynamic Values and Equilibrium Concentrations for the Reaction $\tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightleftarrows OH^\bullet$

temp, K	ΔH_r, kcal/mol	ΔG_r, kcal/mol	K_p, atm	$OH^\bullet$, concn,[a] molecule/cm^3
1000	38.87	28.73	5.3×10^{-7}	8.06×10^{9}
1100	38.90	27.71	3.1×10^{-6}	8.66×10^{10}
1200	38.92	26.69	1.4×10^{-5}	3.50×10^{11}
1300	38.94	25.67	4.8×10^{-5}	1.13×10^{12}
1400	38.95	24.65	1.4×10^{-4}	3.09×10^{12}
1500	38.96	23.63	3.6×10^{-4}	7.33×10^{12}

[a] For calculating the $OH^\bullet$ radical concentration the pressures of H_2O and O_2 were taken to be 3 and 57 mTorr, respectively.

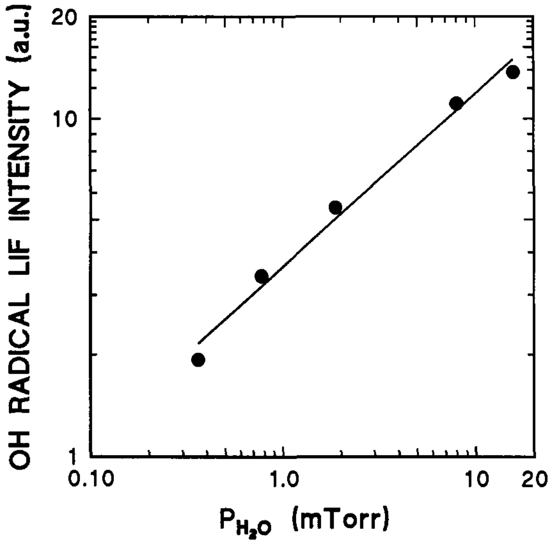

Figure 8. Effect of H_2O partial pressure on the $OH^\bullet$ radical concentration at 1223 K with 16 mTorr of O_2.

Perhaps the most convincing evidence for the equilibrium of reaction 2 is the effect of H_2O and O_2 partial pressures on the $OH^\bullet$ radical concentration. The results obtained by varying the H_2O and O_2 partial pressures over La_2O_3 at 1223 K are given in Figures 8 and 9, respectively. The law of mass action would require that, at equilibrium, the concentration of $OH^\bullet$ radicals should vary according to the 1/2 power of the H_2O pressure and the 1/4 power of the O_2 pressure. The experimental values were 0.51 ± 0.04 and 0.26 ± 0.02 for H_2O and O_2, respectively.

Related to the question of chemical equilibrium is the issue of thermal equilibrium. As described by Talley *et al.*,[21] the LIF signals may be converted into relative quantum state populations, from which a rotational temperature may be calculated. In order to significantly populate the higher rotational states, the La_2O_3 catalyst was maintained at 1206 K. The H_2O and O_2 pressures were 3 and 57 mTorr, respectively, with a total pressure of 60 mTorr. The rotational energy distribution, shown in Figure 10, enables one to calculate T_r for the desorbing radicals. Even at these low pressures, however, some of the $OH^\bullet$ radicals will have undergone collisions, which increases the population of the lower rotational states. Therefore, only rotational levels higher than $J = 5$ were used to determine $T_r = 1230 \pm 75$ K. Clearly, within experimental error it can be concluded that the $OH^\bullet$ radicals are in thermal equilibrium with the surface. This equilibration may

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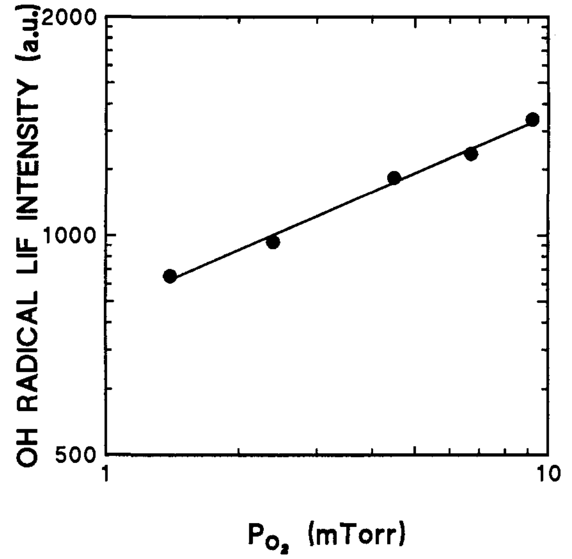

Figure 9. Effect of O_2 partial pressure on the OH• radical concentration at 1193 K with 1.8 mTorr of H_2O.

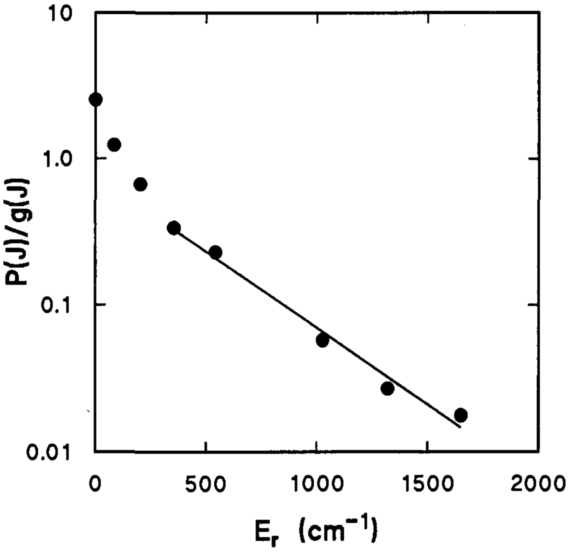

Figure 10. Rotational population distribution for OH• radicals over La_2O_3 at 1206 K with 3 mTorr of H_2O and 57 mTorr of O_2.

occur either prior to desorption or as a result of subsequent collisions as the radicals diffuse through the layer of catalyst particles.

Discussion

The relative rates of OH• radical formation during the oxidation of methane over the four lanthanide oxide catalysts are in good agreement with the relative rates of CH_3• radical formation previously reported, *viz.*, $La_2O_3 > Nd_2O_3 \gg Yb_2O_3 \approx CeO_2$.[10] This correlation suggests that the same type of active center which is responsible for abstracting a hydrogen atom from CH_4 is also capable of abstracting a hydrogen atom from H_2O. The interpretation is complicated somewhat by the fact that the production of OH• radicals is thermodynamically (*i.e.*, equilibrium) limited, whereas the production of CH_3• radicals is limited by kinetics. The formation of OH• radicals during the oxidation of CH_4 is governed by the amount of H_2O produced at the surface. In the previous catalytic studies, which were carried out at 600 and 700 °C, Nd_2O_3 was more active than La_2O_3 by a factor of *ca.* 1.7.[10] But the more basic La_2O_3 is also more subject to poisoning by CO_2 at these lower temperatures than is Nd_2O_3, and at 900 °C La_2O_3 may well be more active than Nd_2O_3. Although the reaction of CH_4 and O_2 gave a greater concentration of OH• radicals over La_2O_3 than over Nd_2O_3, the results of this study show that if the H_2O and O_2 pressures are the same, the concentrations of OH• radicals over La_2O_3 and Nd_2O_3 are essentially the same (Figure 3). In this case, the formation of OH• radicals, of course, did not depend on the rate of CH_4 conversion to H_2O. By contrast, CeO_2 is a moderately effective catalyst for converting CH_4 to H_2O and CO_2, but it is not effective in the production of either CH_3• or OH• radicals. Presumably, CeO_2 lacks the centers that are responsible for hydrogen atom abstraction. In addition, CH_3• radicals react extensively with the CeO_2 surface.[11,15]

There is substantial experimental and theoretical evidence that surface O^- or O_2^{2-} ions are responsible for the activation of CH_4 on strongly basic metal oxides.[22-26] As noted previously, peroxide ions have been detected on La_2O_3 at temperatures near 1000 K using *in situ* laser Raman spectroscopy. By analogy with the mechanism for the formation of CH_3• radicals,[27] we propose that OH• radicals are produced *via* the following catalytic cycle:

$$H_2O + O_{2s}{}^{2-} \rightarrow OH^{\bullet} + HO_{2s}{}^{2-} \qquad (3)$$

$$H_2O + HO_{2s}{}^{2-} \rightarrow OH^{\bullet} + 2OH_s{}^{-} \qquad (4)$$

$$2OH_s{}^{-} \rightarrow H_2O + \square + O_s{}^{2-} \qquad (5)$$

$$^{1}/_{2}O_2 + \square + O_s{}^{2-} \rightarrow 2O_{2s}{}^{2-} \qquad (6)$$

Here, "□" refers to an oxygen vacancy, and the subscript "s" refers to surface species. It is possible that peroxide ions are in equilibrium with O^- ions:

$$O_{2s}{}^{2-} \rightleftarrows 2O_s{}^{-} \qquad (7)$$

in which case, reaction 3 could be replaced by

$$H_2O + O_s{}^{-} \rightarrow OH^{\bullet} + OH_s{}^{-} \qquad (8)$$

For the equilibrium of reaction 2 to be achieved, OH• radicals must be converted back to H_2O and O_2 by the reverse of reactions 3 and 6. The probability of gas-phase coupling of OH• radicals within the distances of interest would be small, considering their low concentrations and the need for a third body.

Conclusions

At reagent partial pressures in the mTorr range, the strongly basic lanthanide oxides are capable of generating OH• radicals at the surface. These radicals then emanate into the gas phase. When H_2O and O_2 are reagents, the OH• radical appears to be in equilibrium with the reagents. When CH_4 and O_2 are reagents, H_2O is formed as a product and subsequently reacts with any remaining O_2 to form OH• radicals. The same type of active surface center, probably peroxide ions, is capable of forming CH_3• radicals from CH_4 and OH• radicals from H_2O. The concentrations of the two radical species are comparable during the oxidation of CH_4 under the conditions of these experiments, although this will not generally be the case since the formation of CH_3• and OH• radicals is limited by kinetics and by thermodynamics, respectively.

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