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Effect of CH_4 and CO_2 on the catalytic formation of OH· radicals over La_2O_3

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Surface-generated gas-phase hydroxyl radicals are formed when H_2O and O_2 react over La_2O_3 at 900°C. The addition of CH_4 has a strong, negative effect on the production of these radicals, which is attributed to the competition between CH_4 and H_2O for an active form of oxygen on the surface. At the temperature of these experiments, CO_2 had no effect on the formation of OH· radicals.

Keywords: effect of methane and carbon dioxide on hydroxyl radicals, formation of hydroxyl radicals over lanthanum oxide, catalytic combustion, laser-induced fluorescence of hydroxyl radicals

1. Introduction

Hydroxyl radicals, which may be important chain carriers in catalytic combustion [1,2], are formed when H_2O and O_2 react over the strongly basic lanthanide oxides [3,4]. The OH· radicals emanate into the gas phase where they are detected using laser-induced fluorescence (LIF) spectroscopy. For a series of lanthanide oxides, the order of activity for OH· radical production was found to be $La_2O_3 > Nd_2O_3 > Sm_2O_3 > Yb_2O_3 \gg CeO_2$ [3]. This is the same order as that found for the formation of $CH_3\cdot$ radicals during the reaction of CH_4 with O_2 [5], which suggests that a common type of active center, e.g., O^- ions on the surface, may be responsible for the reactions

$$H_2O + O_s^- \rightarrow OH\cdot + OH_s^- \quad (1)$$

and

$$CH_4 + O_s^- \rightarrow CH_3\cdot + OH_s^- \quad (2)$$

If a common active center were involved, one might expect that the presence of CH_4 would inhibit the formation of OH· radicals. Competition for active centers, as described by reactions (1) and (2), could influence the importance of OH· radicals in catalytic combustion, since CH_4 would be present as a reagent. A secondary issue is the role of CO_2, a product of combustion, as a poison for the generation of OH· radicals. The experiments described here were designed to determine the effects of CH_4 and CO_2 on the formation of OH· radicals over a La_2O_3 catalyst at 900°C.

2. Experimental

The concentration of hydroxyl radicals detected in the gas phase, approximately 5 mm downstream from the catalyst, was determined using LIF spectroscopy. Details of the reaction cell and the LIF system have been described previously [3]. Briefly, the catalyst was deposited onto a quartz frit, located at the terminus of a flow tube, using either a slurry of La_2O_3 in water or an aqueous solution of $La(NO_3)_3$. The $La(NO_3)_3$ was subsequently converted to the oxide by heating the sample to ca. 950°C in 0.5 Torr of flowing O_2 for 12 h. Both preparation methods yielded similar results [3]. The catalyst was heated in situ to 950°C prior to carrying out the reaction at 900°C. Gas mixtures consisting of O_2, H_2O and He were allowed to flow over the catalyst at rates of 9.1, 2.5 and 33 ml/min (STP), respectively. Either CH_4 or CO_2 was added to this gas mixture so as to achieve the desired partial pressure.

As shown previously [3,4], the LIF signal, together with the Raleigh scattering signal from air, can be used to determine the absolute concentration of hydroxyl radicals. The hydroxyl radical concentration near the surface was obtained by extrapolation of the results to a distance 2 mm below the catalyst, using a $1/r$ relationship.

The concentrations of stable species in the effluent gas from the reactor were determined using gas chromatography. The exiting gas stream, at a low pressure, was shunted through a collection port into a sample volume for ca. 30 s. Helium was then added to the collected gas to bring the pressure in the sample chamber up to 1 atm.

3. Results and discussion

Using constant oxygen and water pressures of 280

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and 80 mTorr, respectively, and a nominal total cell pressure of 1.5 Torr, the concentration of hydroxyl radicals formed over various amounts of La_2O_3, as a function of CH_4 partial pressure, was determined. As shown in figure 1, with 15 mg of La_2O_3 and no CH_4 present, the OH· radical concentration was 1.5×10^{11} molecules/cm^3, which is the equilibrium value expected for the reaction

$$\tfrac{1}{2}O_2 + H_2O \rightleftharpoons 2OH\cdot \qquad (3)$$

Based on previous results, it was anticipated that the reaction would approach equilibrium at this temperature and catalyst loading [3]. The near-equilibrium state of the reaction was confirmed by the fact that the OH· radical concentration did not change when the La_2O_3 loading was increased to 30 mg. However, when the catalyst amount was decreased to 4 mg, there was a significant decrease in radical concentration, which indicates operation in a kinetically controlled regime.

The addition of CH_4 to the reaction mixture caused a decrease in OH· radical concentration for all three catalyst loadings, as shown in figure 1. As the CH_4 pressure was increased, the OH· radical concentration decreased to a small, but non-zero, level. The OH· radical signal remained the same amplitude above the background signal, even up to 2 Torr of CH_4. It was previously demonstrated that in the absence of a catalyst no OH· radicals were detected [3]. Clearly, CH_4 interferes with the formation of OH· radicals on the catalyst, or it is responsible for the destruction of the radicals. At least two observations suggest that inhibition of OH· radical formation occurs through competition for a common set of active sites on the surface.

First, the results of adding CH_4 are qualitatively different for the three loadings of La_2O_3. At the largest loading (30 mg), the reaction is at equilibrium, and the negative effect of CH_4 was not evident until its partial pressure exceeded ca. 30 mTorr. At this pressure of CH_4, the competition for sites would be such that the concentration of OH· radicals would fall below the equilibrium level; i.e., a kinetic effect would become evident. When smaller amounts of catalyst were present (4 and 15 mg), the inhibitory effect of CH_4 on OH· radical formation was evident even at 30 mTorr, although with 15 mg of La_2O_3 higher CH_4 pressures were required to decrease the radical concentration because the system was initially near equilibrium.

Second, one must consider the possibility of the gas-phase reaction

$$OH\cdot + CH_4 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_2O + CH_3\cdot \qquad (4)$$

which would result in the destruction of OH· radicals. This is a fast reaction with a rate constant of $k_4 = 3.26 \times 10^{-12}$ cm^3/(molecule s) [6]. But the mean free path for the collision of an OH· radical with a CH_4 molecule is ca. 10 mm for a CH_4 pressure of 30 mTorr. Thus, the effect of reaction (4) would be minimal over the distance of 5 mm between the catalyst and the laser beam. In order to further explore the possible effect of gas phase reactions, the experiment was carried out at lower pressures, for which the mean free path was even greater. As shown in figure 2, the concentration of OH· radicals in the absence of CH_4 was 9×10^9 molecules/cm^3, which may be compared with an equilibrium value of 2.1×10^{10} molecules/cm^3 for these conditions. The

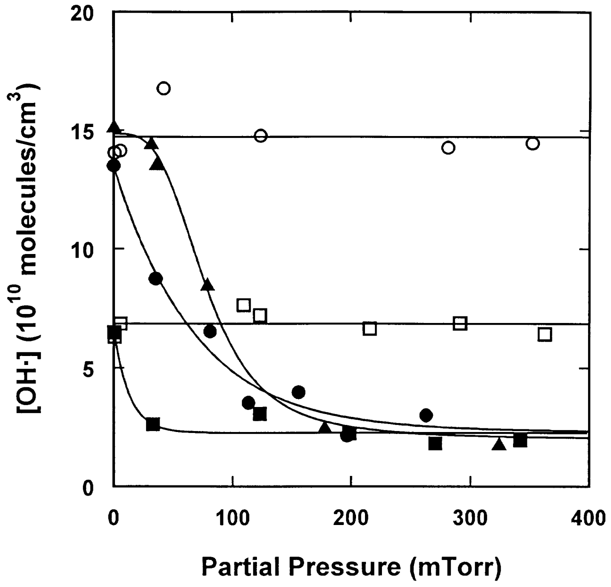

Figure 1. Effect of CH_4 or CO_2 on the concentration of OH· radicals: addition of CH_4 to 4 mg (■), 15 mg (●) and 30 mg (▲) La_2O_3; addition of CO_2 to 4 mg (□) and 15 mg (○) La_2O_3. Partial pressures were 80 mTorr H_2O, 280 mTorr O_2 and 1000 mTorr He.

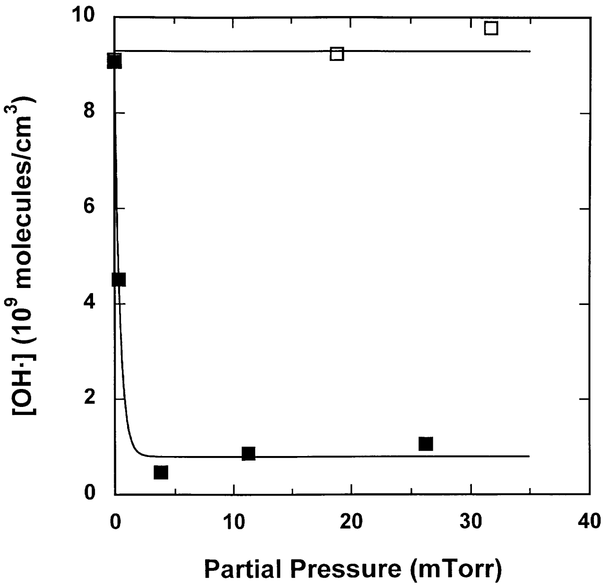

Figure 2. Effect of CH_4 or CO_2 on the concentration of OH· radicals: addition of CH_4 (■) or CO_2 (□) to 4 mg La_2O_3. Partial pressures were 7.7 mTorr H_2O, 27 mTorr O_2 and 98 mTorr He.

same negative influence of CH_4 was observed as when the nominal total pressure was 150 mTorr. The OH· radical concentration decreased by more than 50% with only 1 mTorr of CH_4 in the gas stream. The mean free path for OH· radicals colliding with CH_4 at 3 mTorr would be ca. 100 mm, which is, of course, much longer than the distance between the catalyst and the laser beam.

Although gas phase reactions between OH· and CH_4 are probably not significant, it is conceivable that surface reactions may be important. One should recognize, however, that La_2O_3 is a closed shell oxide and the heat of adsorption of either species is expected to be small. Moreover, entropy effects at 900°C would be unfavorable for adsorption. Mirodatos and co-workers [7] have demonstrated that CH_4 is not adsorbed on La_2O_3 at 650°C. At the low pressures of these experiments, it seems unlikely that surface reactions between adsorbed OH· and CH_4 would be responsible for the observed results.

Another point to be considered in the interpretation of the results of figures 1 and 2 is the loss of O_2 and CH_4 due to catalytic conversion over the La_2O_3 and the possible effect of CO_2 that is produced during such a combustion reaction. The CH_4 conversions were determined over 4 mg of catalyst under conditions comparable to those used to obtain the data reported in figure 1, and the results are shown in figure 3. At 900°C, the CH_4 conversion was less than 10% for a CH_4 partial pressure of 167 mTorr. It appears unlikely, therefore, that CH_4 combustion would have a significant influence on the results of figure 1, except perhaps at the largest catalyst loading and the extremes of low and high CH_4 concentrations. For example, one could argue that the results obtained with 30 mg of La_2O_3 and at small partial pressures of CH_4 (figure 1) could result from the reaction of most of the CH_4 due to complete oxidation. Nevertheless, the negative effect of CH_4 on OH· radical concentration is evident under conditions such that the conversion of CH_4 would be small.

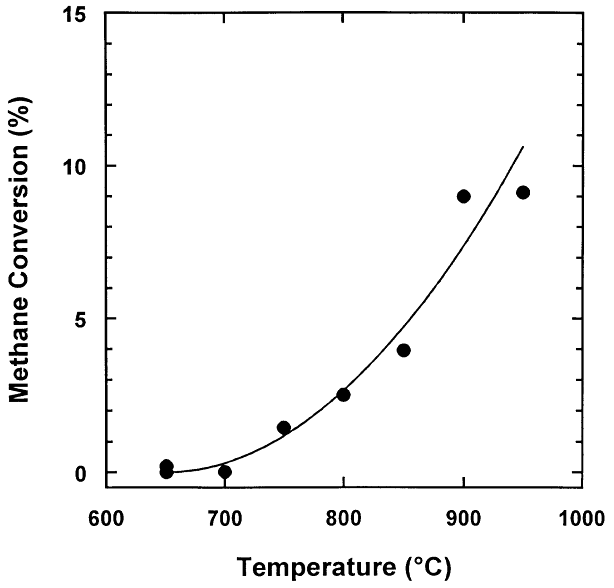

Figure 3. Methane conversion over 4 mg La_2O_3. Partial pressures were 7.7 mTorr H_2O, 27 mTorr O_2 and 98 mTorr He.

The issue of CO_2 poisoning was addressed by adding this gas, rather than CH_4, to the reactants, and the results are shown in figures 1 and 2. At 900°C, CO_2 had no detectable effect on the formation of OH· radicals. Thus, CO_2 produced during the partial oxidation of CH_4 did not influence the results.

The negative effect of CH_4 on the production of OH· radicals over La_2O_3 can best be understood in terms of the competition of H_2O and CH_4 for active centers, as described by reactions (1) and (2). Previous results confirmed that CH_3· radicals and OH· radicals were produced at comparable rates when CH_4 and O_2 were reacted over La_2O_3 at 960 °C [4]. The OH· radicals were derived from the H_2O produced during the partial oxidation of CH_4. When H_2O was added to the system in place of CH_4, there was a marked increase in the production of OH· radicals. We now realize that this increase was, in part, a result of the competition for active centers when CH_4 was present.

It is interesting to note that even at large partial pressures of CH_4, the OH· radical concentration reached a constant level and did not decrease to zero (figures 1 and 2). This observation suggests that there may be two sets of active sites that are responsible for OH· radical formation. Methane competes with water on one set, but on the other, less significant set it does not.

Finally, one should consider the consequences of these results on the role of surface-generated gas-phase hydroxyl radicals in the catalytic combustion of CH_4. A previous model calculation indicated that concentrations of OH· radicals produced over the catalyst via reaction (3) are greater than those that might be expected during a gas phase combustion reaction [3]. In the calculations, however, it was assumed that equilibrium concentrations of OH· radicals from reaction (3) were achieved. The negative effect of CH_4 now needs to be addressed, although the results of figure 1 suggest that with a large amount of catalyst the concentration of OH· radicals could approach equilibrium, even in the presence of CH_4. The practical significance of these competitive reactions can best be evaluated by carrying out similar experiments at much higher pressures. Such experiments are not possible with our present LIF system, but a recently developed technique known as cavity ring-down spectroscopy would enable one to obtain similar data at atmospheric pressure [8,9].

4. Conclusions

Over La_2O_3 at 900°C, CH_4 competes with H_2O for active sites on the surface and thereby decreases the rate of OH· radical formation. By contrast, CO_2 has no effect on the rate of radical formation. The role that surface-generated gas-phase OH· radicals play in catalytic combustion may be affected by the presence of CH_4 as a reagent.

Acknowledgement

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References

[1] L.D. Pfefferle, T.A. Griffin, M. Winter, D.R. Crosley and M. Dyer, J. Combust. Flame 76 (1989) 325.

[2] D.G. Vlachos, L.D. Schmidt and R. Aris, AIChE J. 40 (1994) 1005.

[3] K.B. Hewett, L.C. Anderson, M.P. Rosynek and J.H. Lunsford, J. Am. Chem. Soc. 118 (1996) 6992.

[4] L.C. Anderson, M. Xu, C.E. Mooney, M.P. Rosynek and J.H. Lunsford, J. Am. Chem. Soc. 115 (1993) 6322.

[5] K.D. Campbell, H. Zhang and J.H. Lunsford, J. Phys. Chem. 92 (1988) 750.

[6] D.L. Baulch, C.J. Cobos, R.A. Cox, C. Esser, P. Frank, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, R.W. Walker and J. Warnatz, J. Phys. Chem. Ref. Data 21 (1992) 411.

[7] S. Lacombe, H. Zanthoff and C. Mirodatos, J. Catal. 155 (1995) 106.

[8] A. O'Keefe and D.A.G. Deacon, Rev. Sci. Instr. 59 (1988) 2544.

[9] R.T. Jongma, M.G.H. Boogaarts, I. Holleman and G. Meijer, Rev. Sci. Instr. 66 (1995) 2821.