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CO and H_2 oxidation on a platinum monolith diesel oxidation catalyst

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Abstract

This paper presents experimental and modelling results for the oxidation of mixtures of hydrogen and carbon monoxide in a lean atmosphere. Transient light-off experiments over a platinum catalyst (80 g/ft^3 loading) supported on a washcoated ceramic monolith were performed with a slow inlet temperature ramp. Results for CO alone agree with earlier results that predict self-inhibition of CO; that is an increasing light-off temperature with increasing CO concentration. Addition of hydrogen to the feed causes a reduction in light-off temperature for all concentrations of CO studied. The most significant shift in light-off temperature occurs with the addition of small amounts of hydrogen (500 ppm, v/v) with only minor marginal enhancement occurring at higher hydrogen concentrations. Hydrogen alone in a lean atmosphere will oxidise at room temperature. In mixtures of hydrogen and CO, the CO was observed to react first until a conversion of about 50% was observed, at which point the conversion of hydrogen rapidly went from 0 to 100%.

Simulations performed using literature mechanistic models for the oxidation of these mixtures predicted that hydrogen ignites first, followed by CO, a direct contradiction of the experimental evidence. Upon changing the activation energy between adsorbed hydrogen and oxygen, the CO was observed to oxidise first, however, no enhancement of light-off was predicted. The effect cannot be explained by the mechanistic model currently under discussion.

Keywords: Platinum catalyst; Monolith; CO oxidation; Hydrogen

1. Introduction

In spite of many years of use, several aspects of the underlying mechanisms that govern the operation of catalytic converters remain controversial. A better understanding of, for example, the reaction mechanism and resultant rate expressions would be advantageous in helping to design better converters to meet the increasingly more stringent emission control regulations. Further, by understanding the mechanisms, and being able to represent them mathematically, increased use may be made of computer aided design, which will shorten the development cycle and help lead to better design.

We concern ourselves here with the oxidation reactions that occur under the lean burn conditions typically found in a diesel engine exhaust. In this paper, we limit the work to the oxidation of CO in the presence of hydrogen over a platinum catalyst. Although the oxidation of CO over platinum has been thoroughly studied, there is no consensus as to the reaction mechanism. Recently, it was reported that the primary mechanistic models commonly used in the catalytic converter literature cannot adequately explain the observed ignition extinction curves and step functions [1].

Given the recent interest in hydrogen fuel cells with their need for a hydrogen feed with very low CO concentrations, the discussion of CO and H_2 oxidation over Pt catalysts has been dominated by the study of preferential oxidation of CO (PROX) [2–5], where typical platinum catalysts have been shown to oxidise carbon monoxide selectively despite the high concentrations of hydrogen present. While many low-temperature, low-pressure [6], and single-crystal [7] studies have been performed closely studying the catalyst surface, less is known about the system at atmospheric pressure and low hydrogen concentrations. Owing to the scarcity of good kinetic parameters for CO and H_2 oxidation, kinetic parameters are

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frequently taken from other sources, such as the PROX studies, and applied to automotive catalyst simulations [8]. It has been reported that CO inhibits the ignition of H_2, and H_2 promotes the ignition of CO [9–11]. The inhibition of hydrogen oxidation by CO has been attributed to competitive adsorption [12], while hydrogen promotion of CO oxidation has been attributed to various effects. Different proposals exist in the literature, and the debate remains open.

Sun et al. [9] measured the temperature response of a monolith to step changes in inlet CO and hydrogen concentration. The monolith had a Pt/Al_2O_3 washcoat, and temperatures were measured along the centreline. Their experiments showed that at a particular temperature, increasing the CO concentration led to self-inhibition and extinction of CO oxidation at a critical concentration. In the presence of hydrogen, the CO bifurcation points were shifted to higher CO concentrations, showing that hydrogen assists the ignition of CO. These effects were attributed to the exotherm from hydrogen combustion increasing the temperature of the catalyst, shifting the CO adsorption–desorption equilibrium. The concentrations of hydrogen used in their study ranged from 0 to 2.5%, and exotherms were reported to be on the order of 150 °C, much higher than the present work.

Others [10–12] have attributed this promotion effect to hydrogen in the gas influencing the desorption rate of CO. By increasing the rate of CO desorption, the turnover of surface sites increases, affording other components more opportunites to adsorb. However, the reactions are said to proceed via Langmuir–Hinshelwood type reactions instead of via an Eley-Rideal mechanism (between gas-phase and surface components). To the knowledge of the present authors, little experimental evidence of this influence on CO desorption has been reported in the literature. Kahlich et al. were also inconclusive as to whether the effect is due to hydrogen increasing the rate of CO desorption, and also suggested that there may be an interaction between CO on Pt and the hydroxylated alumina support [3].

The discussion of surface reactions between adsorbed CO and hydrogen is relatively new, and holds more promise for a solution. Coupled reactions [3,13] have been proposed, but as yet none have definitively shown the surface mechanism to be the cause of the hydrogen promotion effect.

The objective of this investigation was to perform a detailed experimental study of the combined oxidation of CO and hydrogen under lean conditions. We employed a transient system, because typically transient data are more informative from a viewpoint of establishing mechanisms, and also because the transient behaviour (that is, ignition and extinction curves) are of interest in the catalytic converter community.

2. Experimental apparatus

An apparatus was constructed to allow for transient experiments on a monolith supported catalyst. The apparatus consisted of three main parts: the gas mixing unit, the gas preheater and reactor, and the analyzers. Gas mixtures were prepared from gas bottles of pure gases (Messer Greisheim GmbH). Standard mass flow controllers were used to control and monitor the flowrate of each gas entering the reactor. The catalyst was platinum contained within an alumina washcoat coated onto a ceramic 400 CPSI monolith obtained from Corning Inc. The monolith was 2.54 cm in diameter and 7.62 cm in length. Axial temperature profiles in the reactor were measured using five K type thermocouples inserted into the monolith channels, filling and preventing flow through the channels. Additional thermocouples were placed immediately before and after the monolith to measure inlet and outlet temperatures, respectively. As fewer than 2% of the available channels were blocked by thermocouples, the impact on the flow field is assumed to be small. A pressure sensor (Wagner Mess-und Regeltechnik GmbH) was used to measure the pressure immediately before the catalyst, which was typically between 1.07 and 1.10 bar. Gases were pre-heated to the inlet temperature using a tubular furnace. Static mixers were included in the oven, to enhance the mixing of the gas and to ensure that the gas composition and temperature was homogeneous.

Concentrations of CO and CO_2 in the reactor effluent were measured using IR spectroscopy (MLT unit supplied by Emerson Process Management), and O_2 concentration was measured using a paramagnetic method (also supplied by Emerson Process Management). An H-Sense Hydrogen Monitoring System, an H_2 mass spectrometer, from V&F Analyse und Messtechnik GmbH was used to measure hydrogen concentrations over a range of 0–10,000 ppm H_2. Because water was condensed and removed from the system to prevent damage to instrumentation and was not measured, a hydrogen balance is not available.

A computer control and data logging system was built using National Instruments LabVIEW 7.0. Electronic input/output devices were supplied by Elektro Beckhoff GmbH. Data analysis was performed with MATLAB 7.0.

3. Results

Transient experiments were conducted to measure the ignition curves for various feed concentrations. We present the curves and data for oxidation of CO alone and for mixtures of CO and H_2. In all cases, the ignition point is defined as the inlet temperature at which the outlet conversion is 50%.

3.1. CO oxidation alone

We present first ignition curves for different inlet CO concentrations. In these experiments, the reactor and feed gas had an initial temperature near 350 K. The temperature of the feed gas was then increased at approximately 0.133 K/s from 350 to 623 K, where it was held constant for about 30 min. In similar experiments performed in another work, experiments were performed at much slower heating rates (0.0167 K/s or 1 K/min), and the difference in heating rate (7.5 K/min versus 1 K/min) was not found to be a dominant factor. In all cases the feed contained 6% (v/v) oxygen, with either 500, 1000, 1500 or 2000 ppm of CO. In each case, the start-up procedure was first to flush with nitrogen for 1 min, followed by addition of oxygen, which was allowed to flow for a further minute, and

Table 1
Experimental ignition points for CO in 6% oxygen at a GHSV of 25,000 h^{-1}

ppm CO	Ignition *T* (K)
500	403
1000	426
1500	436
2000	444

finally addition of CO. This condition was held for 8 min before commencing the temperature ramp.

Table 1 gives the ignition points, defined as the inlet gas temperature corresponding to 50% conversion, with temperatures in Kelvin. The ignition curves are shown in Fig. 1. The GHSV for these experiments was approximately 25,000 h^{-1}. It is seen that increasing concentration of CO causes a higher light-off temperature. Computer modelling of these curves using mechanistic models was shown in [1].

3.2. H_2 oxidation alone

Under the flow conditions used in these experiments, hydrogen was converted completely to water at room temperature, which is expected based on the literature [14]. The simulations presented below were repeated in the absence of carbon monoxide, and met this condition for the parameters used here.

3.3. H_2 and CO oxidation

Observations reported here of CO inhibiting H_2 ignition and H_2 promoting CO are consistent with the results reported in the literature [9–12]. Fig. 2 shows the ignition curve for CO in the presence and absence of hydrogen. The results for 1000 and 2000 ppm CO with 500 and 2000 ppm of H_2 are given in Table 2. Note, that the trend with 2000 ppm CO was the same as with 1000 ppm CO. The key new observation is that a small amount of hydrogen enhances significantly the ignition point, but the marginal benefit of additional hydrogen is small. To the knowledge of the authors, this has not been reported in the literature before. In both cases (1000 and 2000 ppm CO) the light-off enhancement with 500 ppm hydrogen is 22 K, but the light-off temperature is only reduced by an additional 3 K with 2000 ppm hydrogen. We also note that hydrogen ignites at the same temperature as the CO when the mixtures were present, as shown in Fig. 3. The experimental results here show CO beginning to oxidise before H_2, consistent with the selectivity

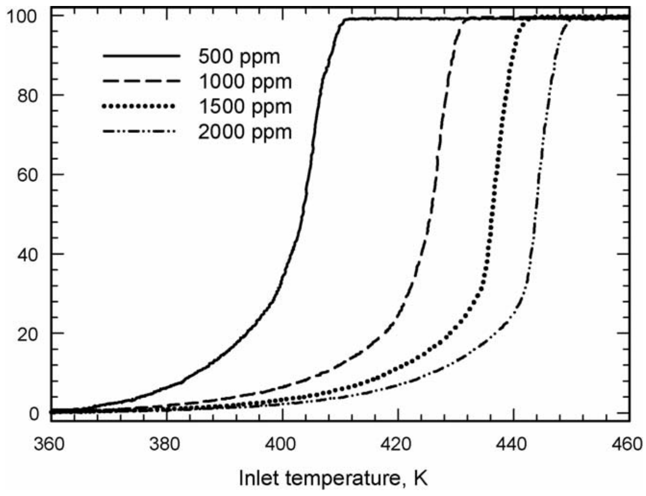

Fig. 1. Experimental light-off curves for different inlet concentrations of CO at a GHSV of 25,000 h^{-1}.

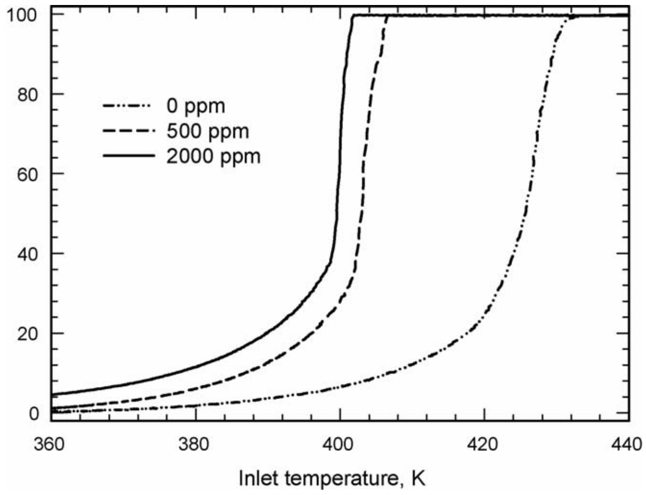

Fig. 2. Experimental light-off curves for different inlet concentrations of H_2 with 1000 ppm CO at a GHSV of 25,000 h^{-1}.

Table 2
Experimental ignition points for CO in 6% oxygen at a GHSV of 25,000 h^{-1}, at 0, 500 and 2000 ppm hydrogen

ppm CO	ppm H_2	Ignition *T*, K
1000	0	426
1000	500	403
1000	2000	400
2000	0	444
2000	500	422
2000	2000	419

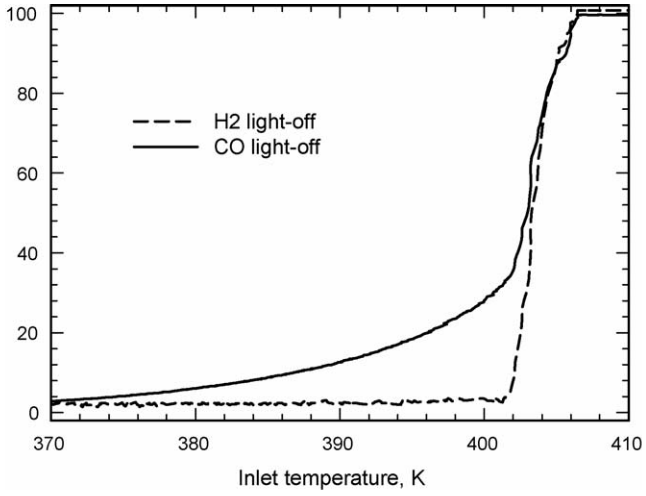

Fig. 3. Experimental light-off curves for a system of 500 ppm H_2 with 1000 ppm CO at a GHSV of 25,000 h^{-1}. CO and H_2 light-off shown.

of Pt toward CO oxidation [5,15,16]. However, once light-off is achieved, and active site turnover increases, total conversion of both species is attained.

4. Discussion

4.1. Effect of H_2 on CO oxidation

The experimental results are in general consistent with other experimental results reported in the literature. Self poisoning of CO oxidation is well known, hence the increasing light-off temperature as concentration increases. Oxidation of hydrogen on a platinum surface in a mixture of nitrogen (~94%) and oxygen (~6%) at room temperature was reported as early as 1823 [14]. For mixtures of CO and hydrogen, the surface of the catalyst is initially predominately covered by CO, which inhibits hydrogen adsorption. We can propose a competitive adsorption between CO and hydrogen, with the rate determining step for reaction being the adsorption of oxygen. As the temperature increases, CO may begin to react, thus opening the surface. At some extent of reaction, sufficient surface is available for significant adsorption of oxygen, and the conversion of CO becomes rapid, and at this point the hydrogen undergoes ignition. It not, however, clear what the mechanism of enhancement of the CO ignition is. It has been proposed that the addition of hydrogen to CO will reduce the light-off point for CO owing to the additional exotherm provided by hydrogen oxidation [9]. However, this proposal is not consistent with our observations. Indeed, since CO is preferentially oxidised before the hydrogen, it is difficult to see how the exotherm could be significant. Secondly, and more importantly, the degree of enhancement cannot be accounted for by the exotherm alone. For example, 500 ppm hydrogen would add only a few degrees to the fluid temperature, yet the light-off temperature was reduced by 22 K. Secondly, if the exotherm alone were responsible, then the addition of 2000 ppm hydrogen should have produced a much lower light-off temperature for CO. The experimental curve in Fig. 4 shows this graphically, where the degree of enhancement does not vary directly with the hydrogen concentration. Therefore, it is proposed that the enhancement must be a function of the surface reaction mechanism.

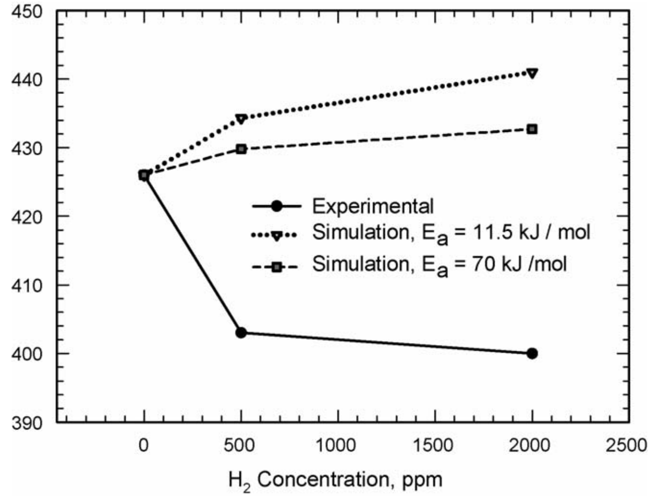

Fig. 4. CO light-off temperature vs. hydrogen concentration for the experimental and simulated (E_a = 11.5 and 70 kJ/mol) light-offs.

4.2. Reaction mechanism

Having raised the issue of reaction mechanism, we will state that it is beyond the scope of the present paper to propose a new mechanism. However, we consider now the current popular mechanisms used in the automotive catalysis literature. It is now generally accepted that the primary route for CO oxidation is via an LH type mechanism, although there are many additional steps required to handle oscillations and CO oxidation over an oxygen covered surface (see Ref. [1]), including a compressed oxygen species that allows CO adsorption to an oxygen covered surface with irreversible oxygen adsorption. It has been shown that a simple LH scheme can account for light-off behaviour from a CO covered surface:

$$CO_{(g)} + \theta_V \rightleftharpoons \theta_{CO} \tag{1}$$

$$O_{2(g)} + 2\theta_V \rightarrow 2\theta_O \tag{2}$$

$$\theta_O + \theta_{CO} \rightarrow CO_{2(g)} + 2\theta_V \tag{3}$$

Where surface component X is defined by θ_X, and free sites are represented θ_V.

The oxidation of hydrogen has several proposed mechanisms in the literature. It is generally considered to proceed by an LH mechanism [17–21], and the following steps have been used in the converter literature [22].

$$H_{2(g)} + 2\theta_V \rightleftharpoons 2\theta_H \tag{4}$$

$$O_{2(g)} + 2\theta_V \rightarrow 2\theta_O \tag{5}$$

$$\theta_H + \theta_O \rightleftharpoons \theta_{OH} + \theta_V \tag{6}$$

$$\theta_{OH} + \theta_H \rightleftharpoons \theta_{H_2O} + \theta_V \tag{7}$$

$$2\theta_{OH} \rightleftharpoons \theta_{H_2O} + \theta_O \tag{8}$$

$$\theta_{H_2O} \rightleftharpoons H_2O + \theta_V \tag{9}$$

Eqs. (4) and (5) show the dissociative adsorption of H_2 and O_2. Adsorbed H and O can form the hydroxyl as shown in Eq. (6). At this point, [18] state that two reaction pathways are possible. Hydrogen addition (Eq. (7)) can occur, forming adsorbed water. Also possible is the hydroxyl disproportionation step, Eq. (8). Harris et al. [23] published an early model that although it did not include the hydroxyl disproportionation step (Eq. (8)), claims that the formation of θ_{OH} (Eq. (6)) is rate-limiting.

4.3. Computer simulations

Using a single channel simulator previously developed [24], the light-off curves for the CO and hydrogen mixtures were modelled. This transient simulator uses elementary kinetic models to calculate the reaction pathways on the catalyst surface. Axial symmetry is assumed. The associated heat and

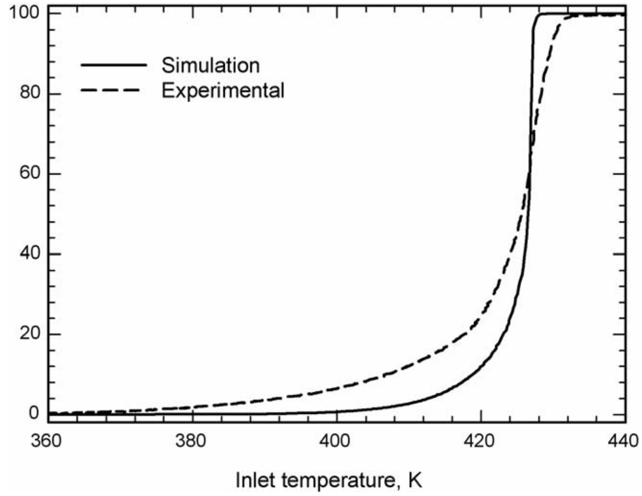

Fig. 5. Experimental and simulated light-off curves for 1000 ppm CO at a GHSV of 25,000 h^{-1}.

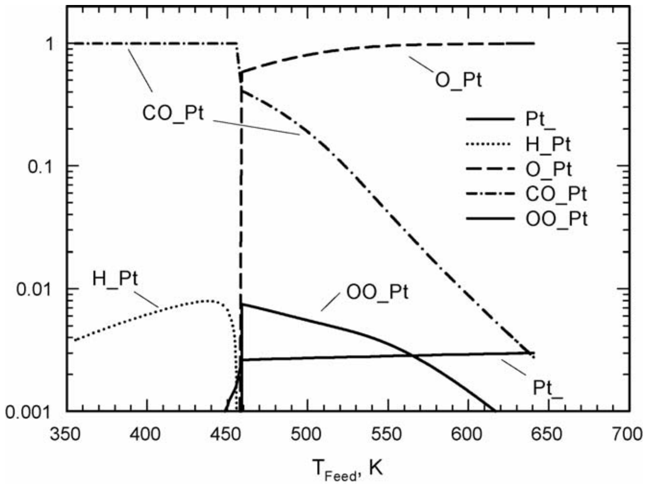

Fig. 7. Surface coverage of various components for the simulated light-off curve of 1000 ppm CO with 500 ppm H_2 using $E_a = 11.5$ kJ mol^{-1}, at the inlet of the reactor. Free sites (Pt_), adsorbed H (H_Pt), adsorbed O (O_Pt), adsorbed CO (CO_Pt), adsorbed compressed oxygen species (OO_Pt).

mass transport equations are also considered, generating a large system of non-linear equations which are solved using the Newton–Krylov method. As before [1], the precious metal loading factor in the model was adjusted to match the experimental CO light-off curves and all other values were taken from the literature. A comparison of the light-off curve for simulation and experiment for 1000 ppm CO alone is shown in Fig. 5. Simulation of the combined case of 1000 ppm CO and 500 ppm hydrogen gave the results shown in Fig. 6. It can be seen that the model predicts that the hydrogen will start to react first, and then the CO will react very suddenly when the hydrogen conversion is complete, and that the light-off of CO is slightly delayed. This phenomenon can be explained in terms of the relative reaction rates and surface coverages. At low temperature, the surface is primarily covered by CO, as shown in Fig. 7, with a small amount of hydrogen. The determining factor for the overall reaction rate is the surface coverage of oxygen. As there are few free sites, as well as the low competitiveness of oxygen compared to carbon monoxide, oxygen adsorption is very slow and the surface coverage is very low. The reaction rates for individual steps calculated at 400 K can be seen in Table 3. However, the literature models give a very high rate for the surface reaction of hydrogen and oxygen, therefore, as soon as oxygen is adsorbed it will immediately react with adsorbed hydrogen. Only when most of the adsorbed

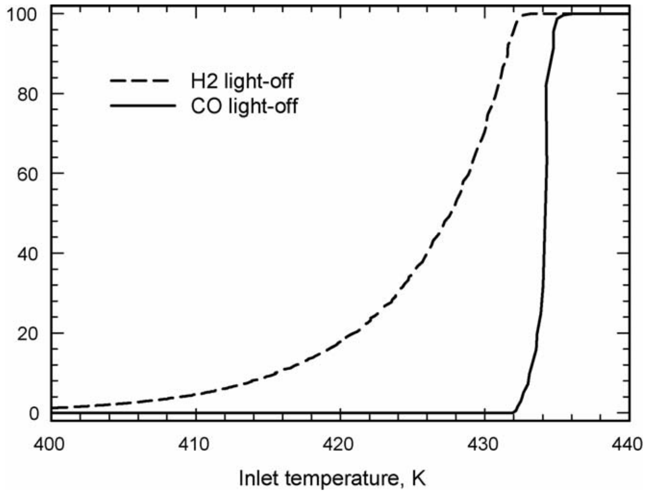

Fig. 6. Simulated light-off curves for 1000 ppm CO with 500 ppm H_2 using literature values for the rate constants.

Table 3
Reaction rates at 400 K, shortly before ignition

Reaction		Rate (mol m^{-3} s^{-1})
1 forward	$CO_{(g)} + \theta_V \rightleftharpoons \theta_{CO}$	8×10^{-3}
1 reverse	$CO_{(g)} + \theta_V \rightleftharpoons \theta_{CO}$	4×10^{-5}
2	$O_{2(g)} + 2\theta_V \rightarrow 2\theta_O$	4×10^{-2}
3	$\theta_O + \theta_{CO} \rightarrow CO_{2(g)} + 2\theta_V$	4×10^{-25}
4 forward	$H_{2(g)} + 2\theta_V \rightleftharpoons 2\theta_H$	8×10^{-4}
4 reverse	$H_{2(g)} + 2\theta_V \rightleftharpoons 2\theta_H$	7×10^{-4}
5	$O_{2(g)} + 2\theta_V \rightarrow 2\theta_O$	See Eq. 2
6 forward	$\theta_H + \theta_O \rightleftharpoons \theta_{OH} + \theta_V$	8×10^{-4}
6 reverse	$\theta_H + \theta_O \rightleftharpoons \theta_{OH} + \theta_V$	6×10^{-15}
7 forward	$\theta_{OH} + \theta_H \rightleftharpoons \theta_{H_2O} + \theta_V$	4×10^{-4}
7 reverse	$\theta_{OH} + \theta_H \rightleftharpoons \theta_{H_2O} + \theta_V$	1×10^{-14}
8 forward	$2\theta_{OH} \rightleftharpoons \theta_{H_2O} + \theta_O$	2×10^{-18}
8 reverse	$2\theta_{OH} \rightleftharpoons \theta_{H_2O} + \theta_O$	7×10^{-18}
9 forward	$\theta_{H_2O} \rightleftharpoons H_2O + \theta_V$	1×10^{-4}
9 reverse	$\theta_{H_2O} \rightleftharpoons H_2O + \theta_V$	0

Surface coverages were $\theta_{CO} = 0.99$, $\theta_{CO_2} = 0$, $\theta_O = 1 \times 10^{-12}$, $\theta_H = 6 \times 10^{-3}$, $\theta_{OH} = 8 \times 10^{-12}$, $\theta_{H_20} = 1 \times 10^{-10}$, $\theta_* = 3 \times 10^{-5}$, as shown in Fig. 7.

hydrogen is consumed, can adsorbed CO react. This leads to an incorrectly predicted selectivity and order of ignition of CO and H_2. To make the model agree with the experimental observations, it is necessary to modify the rate of the surface reaction between hydrogen and oxygen. Völkening et al. [18] stated that above 300 K, the activation energy for this reaction was higher, on the order of 0.52–0.69 eV (50–67 kJ mol^{-1}) compared to a value of 0.13 eV (12.5 kJ mol^{-1}) at temperatures below 170 K. Simulations with an activation energy in the range of 10.5–70 kJ mol^{-1} produced results with different selectivities, but at approximately 70 kJ mol^{-1}, the reaction became selective towards CO oxidation. It can be seen that the CO is now the first species to react, followed by rapid hydrogen ignition once about 50% conversion of CO is achieved. With the modified value, the selectivity towards CO more closely resembles that reported in the literature, correctly predicting the order of ignition as shown in Fig. 8.

The selectivity towards CO oxidation is plotted for the experimental and simulation results in Fig. 9. Selectivity is calculated as the ratio of the rate of consumption of oxygen for CO oxidation to the rate of consumption of oxygen for both CO and hydrogen oxidation. Clearly it can be seen that the literature activation energy predicts the wrong selectivity, and the modified value more closely represents the experimentally observed results. Neglecting the fact that no enhancement effect is observed in the simulation, the direction and shape of the selectivity curve for the simulation with a modified activation energy value more closely resembles that of the experimental result. However, this parameter will require further study to ensure that a new value may be found with better agreement to experimental and literature studies. Due to the stoichiometry and concentrations used, the selectivity towards CO is 0.67 when both CO and H_2 are completely oxidised. Noise in Fig. 9 is a result of measurement and numerical error at very low conversions (less than 1%).

Note, however, that although the order of ignition is now correctly predicted with the modified value, there is no enhancement of CO light-off, as shown in Fig. 4. Indeed, there is nothing in the mechanism to allow for such an effect, except the possibility of an enhancement caused by the reaction exotherm. As noted earlier, this effect is not of sufficient magnitude to give the observed enhancement. The inhibition effect shown in the simulations may be attributed to competitive adsorption.

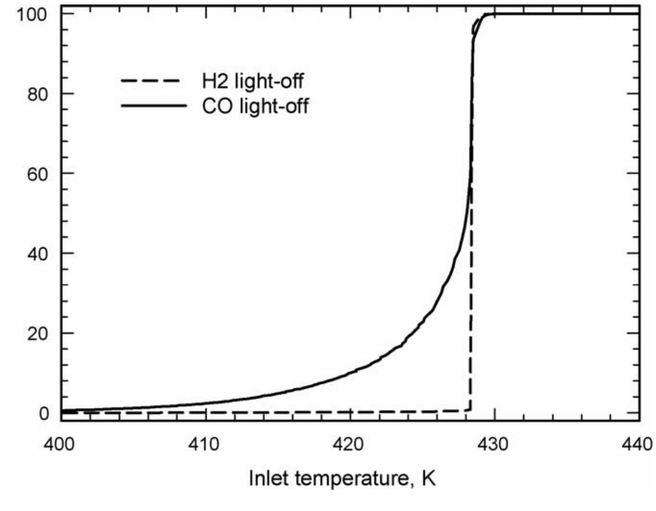

Fig. 8. Simulated light-off curves for 1000 ppm CO with 500 ppm H_2 using slow surface oxidation of adsorbed hydrogen.

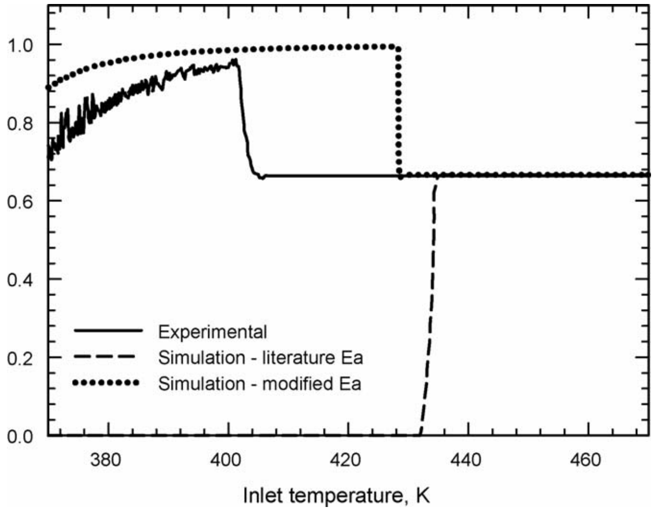

Fig. 9. Selectivity towards CO oxidation for light-off with 1000 ppm CO with 500 ppm H_2. Shown are the experimental, simulation (literature activation energy) and simulation (modified activation energy) values. Due to the stoichiometry and concentrations used, the selectivity towards CO is 0.67 when both CO and H_2 are completely oxidised.

The CO light-off temperature at various concentrations of hydrogen is shown in Fig. 4 for the experiment and simulation results. The simulator appears to be predicting a higher CO light-off temperature with the addition of hydrogen, an effect attributed to competitive adsorption between CO and hydrogen, instead of the experimentally observed enhancement.

Reaction coupling of CO and hydrogen has been proposed by Völkening et. al [18] and Mhadeshwar and Vlachos [19,20], and is considered to be important in determining the inter-relationship between CO and H_2 oxidation.

$$\theta_{OH} + \theta_{CO} \rightarrow \theta_H + \theta_V + CO_2 \qquad (10)$$

Initial attempts to incorporate this step in our mechanism were only able to achieve a very slight enhancement of the order of 1–2 K, however, not the magnitude observed experimentally. Determination of the inter-relationship remains a topic for future work. Indeed, it is not clear that a simple mechanistic explanation is possible.

5. Summary and conclusions

In this work, we have studied the light-off of mixtures of CO and hydrogen under lean conditions. Several conclusions were drawn from this study. Hydrogen was observed to reduce the temperature at which carbon monoxide light-off occurred, while carbon monoxide inhibited the hydrogen oxidation. Carbon monoxide is oxidised first, with hydrogen oxidation occurring when the CO was significantly depleted. The largest enhancement of light-off temperature was achieved at only 500 ppm of hydrogen, and addition of hydrogen up to 2000 ppm gave only a slight further reduction. The release of thermal energy by hydrogen oxidation cannot account for the reduction in light-off temperature of CO. Literature models proposed for the oxidation of CO and hydrogen do not predict the correct order of oxidation or selectivity towards CO unless the parameters are adjusted. After parameter adjustment, they are not able to predict the light-off enhancement. Indeed, it may not be possible to find a simple mechanistic explanation for the observed behaviour. Further studies are currently underway to study the cause of the promotion effect of hydrogen on CO oxidation.

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