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Critical role of water in the direct oxidation of CO and hydrocarbons in diesel exhaust after treatment catalysis

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1. Introduction

With demands for increased fuel efficiency growing, the interest in diesel engines for passenger vehicles has expanded. Diesel engines have, in general, a better fuel economy than standard stoichiometric-burn gasoline vehicles, and emit less CO2. However, there are still emission control issues, specifically associated with NO hydrocarbons, CO, and particulate matter (PM). Currently, diesel oxidation catalysts (DOC) are used to remove hydrocarbons (HC) and carbon monoxide from diesel engines [1] and the DOCs employed can achieve more than 90% reduction in CO and HC emissions at exhaust temperatures higher than ~300 °C [2]. In addition, they also oxidize NO to NO2 which plays an important role in enhancing the performance of downstream catalysts, such as selective catalytic reduction (SCR) catalysts, lean NOx traps (LNTs) and diesel particulate filters (DPFs) [3–6]. Diesel engine exhausts not only comprise HC, NOx, and CO but also H2, O2, CO2 and SO2. In addition, water is also present to concentrations up to 10% and can also play an important role as an oxidant converting CO and HC emissions via water–gas shift (WGS) and steam reforming reactions, respectively, especially at high temperatures [7–10]. It was also reported that the apparent activation energy of the CO oxidation decreased when water was included in the feed. The role of water at low temperature for the enhancement of the CO oxidation activity has been generally recognized as a modification of the catalyst surface and/or the reduction of the self-poisoning of CO [11].

Oh and Hoflund [12] examined the effect of surface water species on hydrous and anhydrous palladium oxide powders under sub-stoichiometric CO oxidation conditions. Therein, XPS results indicated that the water present in hydrous PdO is in the form of the hydroxyl species and as molecular water, which were found to be responsible for CO oxidation at low temperature. Bergeld et al. [13] showed that water was capable of promoting CO oxidation at ~ 200 K through an OH-mediated reaction. Similar conclusions were drawn by Gong et al. [14] who used DFT calculations to investigate CO oxidation in the presence of water on Pt(1 1 1). They reported that, in the presence of water, the CO oxidation barrier could be significantly reduced via the direct reaction of CO plus OH → COOH...
followed by OH mediated decomposition of the COOH forming CO2 + H2O. Furthermore, Parker [15] used inelastic neutron scattering spectroscopy to show that, in the presence of water, two hydroxyl groups were essential for the low temperature oxidation of CO over a model palladium catalyst.

The application of isotope experiments has been extensively described in the literature [16,17] to elucidate the potential role of water in the catalytic oxidation of carbon monoxide over noble metal catalysts. Therein, the use of deuterium oxide and labelled 18O2 helped to confirm that water is directly involved in the conversion of carbon monoxide over Au/Al2O3 catalyst. In some cases water has also been found to have a negative impact on the activity of a diesel oxidation catalyst towards CO oxidation. For example, Lafyatis et al. [18] showed that, using a zeolite 5A water trap before a Pd-PT DOC catalyst, it was possible to reduce the suppression induced by water vapour on the CO light off temperature. Similar inhibition on the activity of Pt catalysts is widely described with the respect to methane combustion [19]. In these systems, the presence of water vapour was found to result in of the formation of inactive hydroxyls groups on the catalyst surface [20]. Cullis et al. [21] also reported that water can react with PdO to form Pd(OH)2 effectively blocking access of methane to the active PdO phase. This effect was also reported by Ribeiro et al. [22].

In the present study, the effect of water on CO and C3H8 oxidation activities under lean conditions was investigated and the reaction mechanism probed using isotope experiments. Understanding these effects are important in order to clarify the reactions which occur over a diesel oxidation catalyst in practical operation.

2. Experimental

2.1. Catalyst preparation

Incipient wetness impregnation was used to prepare Pd/Al2O3 catalyst for CO and HC oxidation studies. The catalyst was prepared with 2 wt% loading using [Pd(NH)2Ac][OH] (Johnson Matthey, Assay 15.3%) as the palladium precursor. SCFa 140 Al2O3 (Johnson Matthey, BET 140 m² g⁻¹, moisture content 2.72% and pore volume 0.42 cm³ g⁻¹) was used as the support. The palladium precursor was weighed and dissolved in 12.5 cm³ water which is just under the pore volume of the amount of support used. This aqueous solution was added dropwise to the required amount of the alumina support, stirring continuously to form a homogeneous mixture. A small amount of water (less than 1 cm³) was then added via a pipette to the catalyst under stirring. The catalyst was dried at 105 °C overnight and calcined at 750 °C for 2 h. BET and CO chemisorption were used to measure the total surface area and the metal dispersion, respectively. The surface area is 130.8 m² g⁻¹ and a Pd dispersion of 16% (particle size 5.9 nm) with an active metal area of 1.6 m² g⁻¹ was found. High resolution transmission electron microscopy (200 kV JEOL-JEM-2010F) measurements were also performed and showed an average Pd particle size of 6.7 nm.

2.2. Activity tests

The catalytic activity tests were carried out in a fixed-bed flow reactor system, consisting of a tubular quartz reactor (i.d. 4 mm). The catalyst sample was sieved to a particle size of 250–300 μm and held in place between plugs of quartz wool. A K-type thermocouple was placed in the centre of the catalyst bed. All the gases were supplied by BOC with the exception of 18O2 which was supplied by CK gases. Each of the gases in the feed system was controlled individually by an Aera™ PC-7700C mass flow controller, connected to an Aera™ ROD-4 controller box. Water was fed by passing Ar through a set of saturators made in-house whose temperatures were controlled by a Grant™ GD120 thermostatic bath. In order to prevent the condensation of water vapour, all the gas lines were trace heated with the temperature of the tapes controlled by Barnstead-Electrothermal™ regulators. The feed gas stream consisted of 1000 ppm CO, 900 ppm C2H6 (as C1), 12% O2, 4.5% H2O (when added), 2 ppm SO2 (when added), 200 ppm NO (when added), 1% Kr (as internal standard) and Ar as balance. The mixture with CO/C2H6/SO2/H2O will be denoted as the “simplified mixture” and the mixture with the addition of NO will be denoted as the “full mixture”, hereafter. The total gas flow rate was 200 cm³ min⁻¹ over 50 mg of catalyst. The catalyst was pre-treated at 140 °C for 1 h using 100 cm³ min⁻¹ Ar. Finally, the reaction gases were introduced to the reactor and the temperature increased from 60 to 300 °C at a ramp rate of 10 °C min⁻¹.

Additional pre-treatment procedures were also applied. The catalyst bed was exposed for 1 h to 900 ppm C2H6 (as C1) in Ar flow, at 100 °C which is below the temperature where propane conversion was achieved. The total flow rate was 200 cm³ min⁻¹.

In order to examine whether water has an active role in the CO and C3H8 oxidation over 2.0wt% Pd/Al2O3 catalyst, activity tests with 18O2 were carried out. The catalytic test was performed using 1000 ppm CO, 900 ppm C2H6 (as C1), 12% 18O2 and 4.5vol% H2O (when added). Further experiments to investigate the isotopic effects on CO oxidation in the presence of D2O over 2.0wt% Pd/Al2O3 catalyst were performed. The reaction mixture consisted of 1000 ppm CO, 900 ppm C3H8 (as C1), 12% 18O2, 4.5vol% H2O (when added), 200 ppm NO (when added).

The evolution of the gas phase species (reactants and products) was monitored by a Hiden™ HPR-20 quadrupole mass spectrometer equipped with a heated quartz inlet capillary. The system is operated by MASSoft software. For the majority of the experiments the following mass to charge ratios were followed as a function of time: 18 (H2O), 27 (C2H6), 28 (CO), 30 (NO), 32 (O2), 44 (CO2), 64 (SO2), 83 (Kr). In the presence of 18O2 the additional species monitored were 46 (C16O16O) and 48 (C18O2).

2.3. Temperature programmed reduction experiments

To determine the number of reducible species on the surface, and the reduction temperature of each reduced species, temperature programmed reduction experiments were performed. The test was carried out by flowing either 1000 ppm CO or 900 ppm C3H8 over 50 mg of sample previously calcined under static air at 750 °C for 2 h. The total flow was 200 cm³ min⁻¹ using 1% Kr as an internal standard and a balance of Ar. The starting temperature was 50 °C and this was increased at a constant rate of 10 °C min⁻¹. The evolution of the gas phase species was monitored by a Hiden™ HPR-20 mass spectrometer, as described above. The mass to charge ratio of the species followed during the catalyst reduction were: 2 (H2), 18 (H2O), 27 (C2H6), 28 (CO), 44 (CO2), 83 (Kr). Each peak marking the consumption of the reducant then corresponds to a different species and the area of each peak is proportional to the amount of reduction which occurs.

3. Results and discussion

3.1. Effect of H2O on CO and C3H8 oxidation

Fig. 1 shows the effect of 4.5 vol% water present within simplified and full gas mixtures on the CO and C3H8 oxidation activity. In the absence of water, with the simplified mixture, 50% conversion of CO and C3H8 was achieved at 153 and 170 °C, respectively. The addition of water to the simplified mixture clearly enhanced the CO oxidation with the temperature for 50% CO conversion decreasing to 100 °C. Moreover, due to the increased CO oxidation activity,
complete conversion of CO was achieved by 140 °C. C3H6 light off also took place at much lower temperatures compared with the dry feed gas stream. However, the addition of water slowed down the propene combustion rate at high temperatures with complete C3H6 conversion achieved at ca. 250 °C in the presence of water compared with ca. 210 °C under dry conditions.

With the addition of 200 ppm NO in the absence of water, the 50% conversion of CO and C3H6 were achieved at 220 and 230 °C compared with 153 and 170 °C in the absence of NO, respectively. These data clearly show the inhibition by NO of the CO and C3H6 activity. In addition, the presence of NO led to a more gradual increase of CO conversion than in the absence of NO, i.e. the light-off curve was sharper in the latter case. However, the presence of 4.5 vol% water also enhanced the CO oxidation even in the presence of NO and thus the temperature at which 50% CO conversion was achieved was 25 °C lower in the wet feed compared with the dry feed in the presence of NO. In contrast, the water only had a small effect on the C3H6 oxidation, as found for the reactions performed in the absence of NO. In this case, the light-off temperature was decreased by only ~6 °C. The promotion effect of H2O on CO oxidation was also studied in the presence and absence of C3H6.

The CO conversion data in the presence and absence of C3H6 are shown in Fig. 2. In the absence of C3H6 and H2O, 50% CO conversion was achieved at 107 °C, whereas in the presence of 4.5 vol% H2O, this decreased by ~10 °C. The presence of co-fed water in the reactant feed resulted in a significant increase in the catalyst activity with the respect to CO oxidation. Similar results were found by Calla and Davis [23] who found that the CO oxidation rate strongly increased upon the addition of water over a Au/Al2O3 catalyst. The addition of 900 ppm C3H6 to the CO/O2 mixture increased the 50% CO light off temperature to 153 °C, showing CO oxidation deactivation by propene probably through competitive adsorption with CO on the Pd sites. Furthermore, when the feed gas stream contained both 900 ppm C3H6 and 4.5 vol% H2O, 50% CO conversion occurred at 100 °C which was similar to the temperature at which the same CO conversion was achieved without H2O. The enhancement of CO oxidation in the presence of water is likely to be the result of an alternative more favourable lower temperature reaction pathway rather than effects due to, for example, competition between water propene for the active sites [24].

Interestingly, as the temperature increased, the decrease in the rate of the CO oxidation due to the presence of propene became more apparent. In this case, the slope of the oxidation curve was found to decrease compared with the CO conversion profile in the absence of C3H6. This variation may be due to changes in the surface concentration of water as a function of temperature which will affect both the rate of both CO oxidation and propene and the extent to which inhibition of the active site plays a role [24]. This is consistent with the conclusions reported by Mhadeshwar and Vlachos [26] who investigated the effect of C3H6 on CO oxidation over a Pt/Al2O3 catalyst. Therein, the inhibition by C3H6 was attributed to competitive adsorption on catalytic sites. A significant loss of activity for CO oxidation is clearly shown on ageing the catalyst in 900 ppm C3H6 (as C1) for 1 h at 100 °C. The dashed line in Fig. 2 shows the effect of this pre-treatment on the CO oxidation from a feed containing 1000 ppm CO, 4.5 vol% H2O and 12% O2 and the feed gas. During propene ageing, no C3H6 conversion was observed. Following the treatment a significant increase in the temperature for 50% CO conversion was observed from 97 to 118 °C. In this case the presence of stable surface species originating from propene adsorption and CO/C3H6/O2 reaction mixture after 900 ppm C3H6 ageing at 100 °C.

3.2. Catalytic role of H2O on CO and C3H6 oxidation

By using isotopically labelled O2, the role of water as a reactive species has been examined. In order to reduce the chance of secondary isotopic exchange reactions occurring with species such as NO and SO2, these experiments were conducted in the absence of NO and SO2. However, as shown in Figs. 1 and 2, the effect of water is similar in the presence and absence of these additional
components. Fig. 4 shows the consumption rate of CO and C3H6 as a function of temperature using 18O2 in the presence of unlabelled water. The production rates of the isotopically labelled CO2 formed upon oxidation reaction with the 18O2 is also shown in Fig. 4. Significantly, the majority of CO2 formed was in the form of C16O2 indicating the importance of oxidation via water rather than dioxygen. A small kink in the C16O2 formation curve was observed at ~140 °C corresponding to the transition where the CO oxidation was complete and C3H6 light off occurred. It is noticeable that C16O18O was only formed during the CO consumption that no significant C18O2 was observed.

C16O2 can be generated via reaction of CO and C3H6 with the water. Due to the low reaction temperatures, it is not likely that water gas shift and hydrocarbon steam reforming are major pathways, since kinetically they would be too slow. Therefore, the formation of C16O2 has to be considered as the result of activation of the CO and C3H6 by H2O/OH. For example in the case of CO oxidation in the presence of water, the gas phase oxygen (18O2 in this case) could scavenge the hydrogen formed from water dissociation and in turn the following reaction pathway may be taking place with OH derived from the dissociative chemisorption of water. The microkinetic model proposed by Mhadeshwar and Vlachos [26] can be used to describe the CO oxidation reaction pathway under H2O condition as reported below:

\[ \text{CO} + \text{OH} = \text{COOH} \]  

Fig. 4. Effect of the presence of water on the CO and C3H6 conversion as function of the reaction temperature. CO2 production signals are also displayed as function of the reaction temperature. Reaction conditions: 1000 ppm CO, 900 ppm C3H6 (as C1), 12% 18O2, 4.5 vol% H2O (when added), 1% Kr (internal standard), Ar to balance a total flow of 200 cm³ min⁻¹.

COOH + OH = CO2 + H2O

(2)

CO and C3H6 can also generate C16O2 via reduction of PdO:

\[ \text{C16O} + \text{Pd}^{16} \rightarrow \text{Pd}^{0} + \text{C16O2} \]

(3)

\[ \text{C3H6} + 9\text{Pd}^{16} \rightarrow 9\text{Pd}^{0} + 3\text{C16O2} + 3\text{H2}^{16} \]

(4)

CO disproportionation reaction is also a possible route to form C16O2; however, no carbon deposition was observed on the catalyst via temperature programmed oxidation measurements following the reaction. A minor contribution is likely to be found from the reduction of PdO. In this case the production of C16O2 would be transient and, therefore, the results shown in Fig. 4 are most likely due to the direct reaction of H2O/OH with CO and C3H6 via reaction intermediates present during the reactions shown in Eqs. (1) and (2). C16O18O may be formed from the oxidation of C16O (from gas phase CO or generated from the reaction of partial oxidation of propene with water) with 18O. It may also be formed from the partial oxidation of propene with 18O forming C18O2 followed by reaction with H218O. However, given that the light off profile matches more closely the propene conversion compared with the CO conversion, it is probable that the latter is the dominant pathway. The doubly labelled carbon dioxide product, C16O2, is uniquely formed from the oxidation C3H6 with 18O2. However, it should be noted, from Fig. 4, that this is a minor route. Fig. 5 shows the CO and C3H6 light off profiles and the evolution of the reaction products under CO/C3H6/18O2 in a dry gas feed. In contrast to the wet gas feed, two regions can be observed. At temperatures below 180 °C the main reaction product was C16O2. In the case of C16O2, two clear peaks were observed at 145 and 180 °C corresponding to complete CO and C3H6 conversion. The formation of C16O2 mainly occurred via CO and C3H6 oxidation using the oxygen from PdO. As the availability of these sites is limited, once the palladium was reduced, the C16O2 and H216O were formed. Above 180 °C, C18O2 was formed due to the oxidation of propene with 18O2.

In order to clarify the reducibility of PdO under either CO or C3H6 flow, temperature programmed reductions were performed with these reductant species. Fig. 6 shows the reduction of PdO using flowing CO. The data confirmed that the PdO was reduced by CO below 200 °C with a sharp CO2 peak observed at 196 °C. In this case, a maximum of ~20% CO conversion was possible via this route. The reduction of the PdO by C3H6 is shown in Fig. 7. Propene was also found to react at ~200 °C leading to CO2 and H2O as the main products. In this case, a maximum C3H6 conversion ~15% was found. Both these features are consistent...
with the peaks observed under dry conditions shown in Fig. 5.

The reaction mechanism of CO oxidation in the presence and in the absence of water is schematically illustrated in Fig. 8.

Fig. 8. Schematic illustration of the predominant reaction pathways for CO oxidation with and without H₂O.

3.3. Isotopic effect of D₂O on CO and C₃H₆ oxidation

Fig. 9 shows the CO and C₃H₆ conversion curves as function of the reaction temperature and the reaction mixture in the presence of H₂O or D₂O.

In contrast with the effect of H₂O, on addition of 4.5 vol% D₂O only a small increase in the catalyst activity towards CO oxidation was observed. For example the temperature at which 50% CO conversion is achieved increases by ~30 °C when D₂O is used compared to the case with H₂O. Moreover, due to the fact that the onset temperature for CO oxidation was increased upon D₂O addition, the onset of C₃H₆ oxidation was also shifted to higher temperatures. This effect is ascribed to the CO remaining on the surface until significantly higher temperatures and inhibiting the propene adsorption.

The differences in catalyst activity with respect to both CO and C₃H₆ oxidation in the presence of D₂O compared with H₂O are indicative of a kinetic isotope effect. Costello et al. [16] investigated the isotopic effect on water enhanced oxidation activity over Au/Al₂O₃ catalyst by using atomic oxygen ¹⁸O and H₂¹⁸O or D₂¹⁸O. Therein, the surface with co-adsorbed ¹⁸O and H¹⁸O₂ was found to consume 24% more CO than the surface with co-adsorbed D₂¹⁸O at 77 K.

Herein, the CO conversion was found to be approximately three times higher in the presence of H₂O compared with D₂O at 100 °C when the simplified oxidation mixture was used. Due to the increased bond strength of O-D versus O-H, activation of the D₂O is reduced compared with H₂O, leading to a lower rate of reaction between hydroxyl groups and CO, for example. The observation of an effect of isotopically labelling the water implies that water activation may be involved in the rate limiting step under our experimental conditions.

4. Conclusions

The results show that the promoting effect of water on CO oxidation is not simply due to changes in surface concentration of the reacting species, i.e. modulating the competitive adsorption effects. Using isotopically labelled dioxygen, the mechanism by which CO₂ is formed in the presence of water has been elucidated and demonstrates that oxidation of CO and propene predominantly occurs via reaction with a water derived species (H₂O or OH) and not with dioxygen. This is likely to occur as a result of H₂O/OH activation of CO and C₃H₆. The observation of the kinetic isotope effect in the CO oxidation reaction performed by using deuterium oxide instead of
water suggests that the activation of water is directly involved in the rate-determining step to form OH groups, which then can react with CO molecules to form CO₂.

These results are important as they indicate that at low temperatures, such as found under cold start conditions, the major pathways for CO and hydrocarbon oxidation in exhaust gases, where water is ubiquitous, involves reaction with water, or a water-related species such as —OH and, consequently, oxygen may play a secondary role. Thus microkinetic modelling of such systems needs to take this into account and not rely on CO/O₂ reaction kinetics only.

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