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Automotive exhaust catalysis under periodic operation

Peter Lewis Silveston *

University of Waterloo, Waterloo, Ontario, Canada

Abstract

Catalytic converters in automobiles now number in the millions. All of these devices are periodically forced about the stoichiometric air–fuel ratio at a frequency of about 1 Hz and a small amplitude. Experiments show that this periodic forcing suppresses rather than enhances conversions under normal operating conditions, even though many publications demonstrate that large rate and conversion improvements do occur for the converter reactions over the individual noble metals used in the three-way catalysts. This review concludes that improvements are not found because enhancement becomes very small in the 400–600°C temperature range and forcing at about 1 Hz is sub-optimal.

1. Introduction

Catalytic converters for automobile exhausts and their control systems are a remarkable achievement. There are currently several million in service and they function under a regime of benign neglect by their owner-operators. They are unique, as well, because the control system subjects the converter to irregular high frequency composition modulation. In addition, the converter often experiences irregular cycles of varying flow-rate and inlet temperature.

In this review we examine the research literature on the periodic operation of the catalytic converter. This topic is interesting from various standpoints. First of all, experimental results demonstrate that cycling of the A/F ratio affects conversion of the primary target species CO, hydrocarbons and NO in the catalytic converter. We will address the question of why is this so? Even though effects of cycling are seen in converters, they appear to be much smaller than those observed when, for example, only CO oxidation is examined. The ultimate questions for this review are: does composition modulation improve catalytic converter performance and, if not, can changes be made that will make this unavoidable modulation beneficial?

1.1. The catalytic converter and the source of composition modulation

Unlike a chemical plant, an automotive vehicle operates routinely under a variety of conditions: for a vehicle, these are cold start, acceleration, deceleration, idle, and constant speed cruising. The three-way catalyst (TWC) and exhaust gas recirculation systems are capable of controlling emissions in the constant speed cruising periods, but are less satisfactory in other types of vehicle operation. What is remarkable about the catalytic converter is that it operates on just 0.5 to 2% of the exhaust gas. Temperatures of the gas entering the catalyst bed approach 1000°C and space veloc-

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* Corresponding author.

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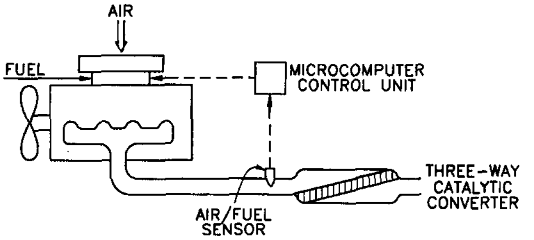

Fig. 1. Schematic of a three-way catalytic converter, oxygen sensor and the A/F ratio feed back control loop (Adapted from Herz [2] with permission of the American Chemical Society, the copyright holder).

ities reach over 100000 h^{-1} when a vehicle operates at full throttle. Cyclic discharge of the engine cylinders means that both flow and temperature oscillate at a high frequency. A review [1] gives further details of the exhaust condition and composition.

Three overall reactions occur in the catalytic converter:

$$2CO + O_2 \rightarrow 2CO_2 \quad (1)$$

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O \quad (2)$$

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \quad (3)$$

In reaction (2), C_3H_6 represents a number of different hydrocarbons, while in reaction (3) NO denotes several nitrogen oxides. Other reactions occur as well, for example N_2O can form, but they are not significant. Composite catalysts incorporating noble metals impregnated on to a high surface area, temperature resistant alumina are universally used. In some cases, transition metal oxides are added.

To meet the requirements of low pressure drop, catalytic converters are either a shallow bed of catalyst pellets, 5 to 15 layers in depth with downflow through the bed, or a catalyst coated monolith consisting of an array of parallel channels, ca. 3 to 8 channels/cm, with flow through the channels in a horizontal orientation. The shallow bed design is indicated schematically in Fig. 1.

Pellets are made by impregnating high surface area γ-Al_2O_3 with dilute metal salts so that the catalytically active components are deposited as an 'eggshell' just below the pellet outer surface. The monolith supports have thin walls with low porosity so a washcoat of γ-Al_2O_3 is applied prior to the impregnation step. Current catalysts, in the active, reduced state, are mixtures of the noble metals: platinum (Pt), palladium (Pd) and rhodium (Rh). Some formulations add transition metal oxides to increase oxygen storage capacity. Roles of the metals are well established. Pt catalyses CO and HC oxidation, but it is essential for paraffin oxidation. Pd is a more active CO, olefin and oxygenate catalyst than Pt, but it has poor tolerance for poisons. Rh improves the NO reduction ability of the catalyst.

The three-way catalyst functions efficiently only in a narrow range of the exhaust gas composition or A/F ratio; thus the converter requires a control system to maintain the A/F ratio within the desired range. A schematic of this system is given in Fig. 1. The sensing device measures the oxygen partial pressure in the exhaust. Its active element is a solid electrolyte consisting of zirconium oxide doped with various other oxides. The sensor signal is periodically monitored by the control unit which initiates a change in the A/F ratio depending on signal magnitude. This system maintains a stoichiometric A/F ratio under constant speed operation and stays remarkably close to this value even when abrupt changes in motor rpm occur.

Sensor hysteresis, measurement and flow lags result in a low amplitude oscillation of the A/F ratio even under constant motor speed. Because of the A/F ratio–composition relationship, the fluctuating A/F ratio caused by the feedback control loop results in time-varying exhaust concentrations. Variations in the CO concentrations measured in situ by Herz [2] at the converter inlet are shown in Fig. 2. The amplitude is about 0.5 for a time-average concentration of 0.75 vol.-%,

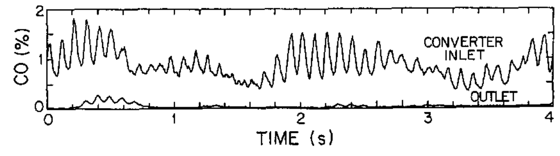

Fig. 2. Time record of catalytic converter inlet and outlet CO concentrations for an exhaust from an automotive engine under A/F ratio feedback control (Adapted from Herz [2] with permission of the American Chemical Society, the copyright holder).

but depends on the A/F ratio and other motor operating conditions. There is a regular 0.5 Hz oscillation and an irregular oscillation at about 10 Hz, but this higher frequency is damped out in the converter. Not evident in the figure are 0.01 to 0.1 Hz oscillations caused by variations in motor speed and throttle control.

1.2. Objectives of composition modulation research on automotive exhaust

A central question in past research is whether the composition modulation caused by feedback control enhances or depresses pollutant conversion. Secondary questions are: (1) conditions under which enhancement is observed, (2) magnitude of enhancement, and (3) sources of improved performance if improvement indeed occurs. Answers to these questions have been sought in three ways. The first has been to focus on CO, the largest pollutant by volume, and examine how its oxidation is influenced by cycling under various conditions of temperature, gas composition and diffusion interference. Presumably, once the effect of modulation on CO oxidation has been established, other oxidation reactions and NO reduction would be explored. The second approach has been to consider all the reactions together and compare behaviour under composition modulation and steady-state operation. The shortcoming of this approach is that it is difficult to explain the experimental observations. The third approach is to seek answers to the questions in steps by considering first the influence of composition forcing on single reactions, then on two reactions together and finally on the complex simultaneous oxidation and reduction reactions that are occurring in the converter. The last approach was chosen by Toyota researchers [3–8].

2. Does the A/F modulation affect conversion?

The answer to this question can only be affirmative. Fig. 3 plots CO and NO conversion versus switching time or 1/2 the cycle period, τ [9]. Data used in this plot were obtained in an integral reactor packed with a platinum catalyst at a mean bed temperature of 525°C and a SV of 104000 h^{-1}(STP) using a simulated exhaust without hydrocarbons. The plot shows conversion increasing as cycle period decreases. At a switching time of 0.1 s, mixing in the converter has smoothed the composition variation sufficiently so that the converter operates almost at steady state. In this experiment, A/F modulation suppresses pollutant conversion.

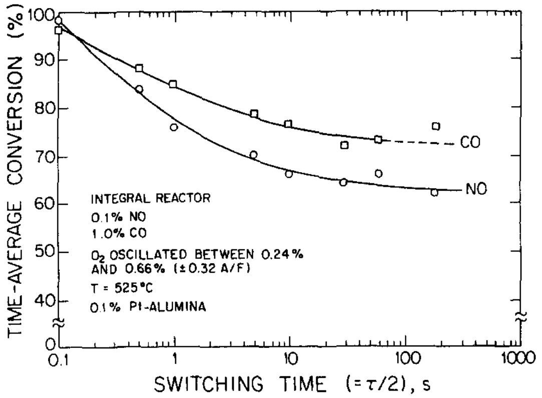

Fig. 3. Time-average CO and NO conversions under periodic forcing of the O_2 concentration as a function of switching time for a 0.1 wt % Pt/γ-Al_2O_3 catalyst in an integral reactor (mid point temperature = 525°C) (Adapted from Hegedus et al. [9] with permission of the American Chemical Society, the copyright holder).

The negative effect of modulation has been observed often. Hegedus et al. [10] screened various Pt–Rh–Pd–Ce formulations, supports and impregnation patterns. One of the screening tests was to compare CO and NO conversions at different amplitudes and frequencies in A/F cycling. More extensive forcing tests were performed with the Ce component because cerium oxide was believed to provide oxygen storage thought necessary for high CO and HC conversion during A/F modulation. Hegedus et al. found that conversions under modulation around the stoichiometric number (SN) were always less than steady-state conversions for Pt/Rh and Pt/Pd/Rh catalysts with and without Ce. The exception was hydrocarbon conversion with exhaust-aged catalysts. The presence of cerium increased HC conversion under modulation. A number of papers

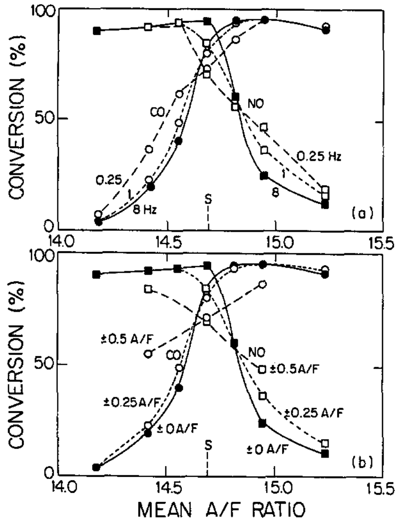

Fig. 4. CO and NO conversion as a function of the time-average A/F ratio under modulation of the A/F ratio for a Pt/Rh catalyst at 550°C and a SV = 52,000 h^{-1}: (a) effect of frequency at an amplitude of ±0.25 A/F, (b) effect of amplitude at a frequency of 1 Hz (Adapted from Schlatter et al. [17] with permission of the American Chemical Society, the copyright holder).

discuss catalyst performance with cerium under A/F modulation [2,11–14]. Cerium improves conversion under cycling, but when measurable, conversion was still below that achieved under steady-state operation at or near the stoichiometric A/F ratio. Most of the Herz and co-worker contributions [2,12–16] used, however, a feedback controlled engine for which steady state could not be attained.

On the other hand, a number of laboratory simulations of catalytic converters have shown that A/F modulation leads to higher conversions under some operating conditions. Schlatter et al. [17] used a simulated automotive exhaust with a Pt/Rh catalyst to examine how modulating the A/F ratio affects CO, HC and NO conversions at 550°C and a SV of 52000 h^{-1}. The results (Fig. 4) show the influence of cycle frequency and cycle amplitude on CO and NO conversion over a range of A/F ratios. '*S*' indicates the stoichiometric A/F ratio where the stoichiometric number is 1.0. In Fig. 4a, conversions are given for a ±0.24 A/F variation. The curve for 8 Hz represents steady state, whereas in the bottom figure which gives the effect of amplitude at 1 Hz, the ±0 A/F curve also represents steady state. Both figures demonstrate that on the rich side of the stoichiometric A/F ratio, CO conversion increases under modulation, while on the lean side, modulation has a similar effect on NO conversion. In either case, decreasing the frequency or increasing the cycle amplitude raises conversion. However, both figures indicate that CO and NO conversions at the stoichiometric A/F ratio decrease with A/F cycling. The decrease depends on the frequency and amplitude. This is consistent with the experiments discussed above. Hydrocarbon conversions are not shown in Fig. 4. Cycling results in lower conversions than at steady state.

Toyota researchers [6,18] report experiments similar to those of GM Research [17], but with the individual noble metals used to make up typical three-way catalysts. Conversion enhancement under modulation was observed away from the stoichiometric A/F ratio for all of the three metals, Pt, Pd and Rh, but for Pt alone, both Yokota et al. [18] and Muraki et al. [6] found that A/F forcing enhanced NO, CO and HC conversion at the stoichiometric ratio. The term enhancement is the ratio of conversion (or rate) under modulation to that under a comparable steady state. Enhancement will be represented by Ψ when the comparable steady state is at the time-average feed composition and by Ψ^* when it is the optimal steady state. In the latter case, we refer to Ψ^* as the global enhancement.

A surprise in Fig. 4 is that remarkably large enhancements of the CO oxidation rate reported in the literature [19] were not observed. Working with supported Pt, Pd and a platinum–tin alloy (Pt–Sn), Gulari and co-workers [20–25] investigated the effect of CO and O_2 modulation on the oxidation rate using a differential packed bed or monolith reactor. Their experiments extended to forcing at 0.2 Hz, but their temperatures were low, 80 to 150°C, relative to automotive exhaust. For each of the three catalysts, they observed large increases in oxidation rate for specific combinations of forcing parameters. These increases reached up to 10 times the rate under steady state for supported Pt and a Pt–Sn alloy, and more than 40 fold for supported Pd. Fig. 5 compares the max-

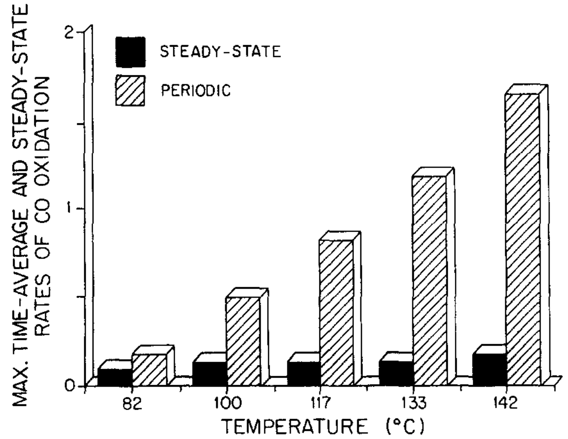

Fig. 5. Comparison of optimal time-average and optimal steady state CO oxidation rates for different temperatures (Reprinted from Vaporciyan et al. [25] with permission of Elsevier Science Publishers B.V., the copyright holder).

imum observed oxidation rate with $CO–O_2$ modulation to the rate at steady state for the identical space velocity [25]. Indeed, in all their experiments, Gulari and co-workers found that composition modulation increased reaction rates over those observed at steady state.

Why is the behaviour under composition modulation different for CO oxidation and for a simulated automobile exhaust for apparently the same catalyst? There are many possibilities: space velocity or degree of conversion, temperature, catalyst composition, particle size and porosity, interference through competing reactions, and the cycling parameters used. In the remainder of this review, we will try to answer our question. In this way we will also answer the ultimate questions: is forced modulation beneficial and, if not, can it be made beneficial?

3. Studies on CO oxidation over noble metal catalysts

Experimental studies and modelling, underway since the early 1970's, are summarized in a recent review [19]. The experimental work may be divided into low temperature (ca. 50 to 150°C) and high temperature (> 300°C) groups. The measurements of Gulari and co-workers, mentioned in the previous section, are typical of the low temperature group. Most were conducted at high space velocities and low conversion, whereas most studies of catalytic converters are carried in integral reactors at high conversion. The amplitude in composition modulation, measured as a CO or O_2 concentration, remains about constant in a differential reactor, but decreases as conversion increases when an integral reactor is used. Amplitude is important in composition forcing and it is usually observed that the modulation effect increases with amplitude. Thus, conversion in an integral reactor such as a packed bed can be expected to be lower than conversion in a differential reactor with the same forcing amplitude and frequency.

The high temperature CO oxidation results under modulation suggest that conversion is the only explanation of differences in performance evident in the literature. Toyota researchers [3] investigated the periodic composition forcing of CO oxidation over the three noble metal catalysts (Pt, Pd and Rh) supported on a low surface area (11 m^2/g) α-Al_2O_3. Most experiments were performed on catalysts containing 0.006 wt.-% metal which approximates the total metal loading in several commercial TWCs. Particle size was 2 mm, but the low surface area probably limited diffusional interference. Catalyst particles were contained in a packed bed and conversions were large except at the lowest temperatures used. Fig. 6 compares the time-average CO conversion with the steady-state conversion at the time-average feed composition (1.33 vol.-% CO and 0.665 vol.-% O_2) for forcing frequencies of 0.5 to 5 Hz and 3 temperature levels. Composition forcing was symmetric ($s = 0.5$ where s is the cycle split) and $SN = 1$ was maintained. SN, the stoichiometric number, is defined for CO oxidation as,

$$SN = 2O_2/CO$$

where O_2 and CO represent concentrations, mol fractions or volumetric flow-rates. When NO and hydrocarbons are present, the definition becomes

$$SN = (2O_2 + NO)/(CO + HC/2)$$

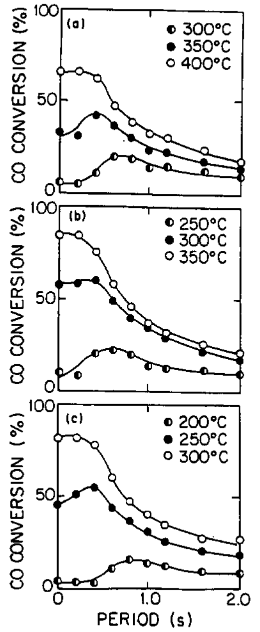

Fig. 6. Effect of cycle period and temperature on CO conversion over (a) Pt, (b) Pd, (c) Rh catalysts with cycling at SN = 1 (Adapted from Muraki et al. [3] with permission of Nippon Kagaku Kaishi, the copyright holder).

Like the A/F ratio, the stoichiometric number represents the oxidizing/reducing condition of the feed mixture. In the Muraki et al. [3] experiments, amplitude was 0.665 vol.-% for CO and 0.3325 vol.-% for O_2; the space velocity was held constant at 30000 h^{-1}. Fig. 6 shows that at the lowest temperature used, periodic forcing gave a 2-to 2.5-fold conversion enhancement for all three noble metal catalysts. This is a large change and it occurs for a stoichiometric mixture. CO–O_2 modulation of catalytic converters with a simulated automobile exhaust suppressed CO conversion. Increasing temperature sharply decreased enhancement. For palladium (Pd), enhancement all but disappears. A further increase of 50°C eliminates the conversion advantage for modulation for all the catalysts. The figure also shows that cycle periods corresponding to the maximum conversion enhancement decrease with temperature.

Data from Fig. 6 have been combined with low temperature CO oxidation data and plotted in Fig. 7. The low and high temperature data for the optimal cycle period, which maximizes the increase in conversion under cycling, appear to form a single data set for Pt and Pd regardless of the metal loading in the catalyst. The figure indicates that if CO–O_2 modulation is to be beneficial for CO oxidation high cycling frequencies must be used at temperatures above 300°C. If we note that conversion is proportional to the average rate in an integral reactor, which makes it possible to estimate the rate enhancement, the high temperature data of Muraki et al. agree reasonably with the low temperature data for Pt and Pd.

Muraki et al. [5] investigated the effect of the stoichiometric number (SN) and CO concentration on conversion under composition forcing for their Pd catalyst. They observed that as SN increases and the mixture becomes oxidizing, the conversion improvement through modulation disappears. Lowering the SN increases the enhancement through forcing. This is consistent with the observations shown in Fig. 4 for a simulated automobile exhaust and the mixed noble metal cata-

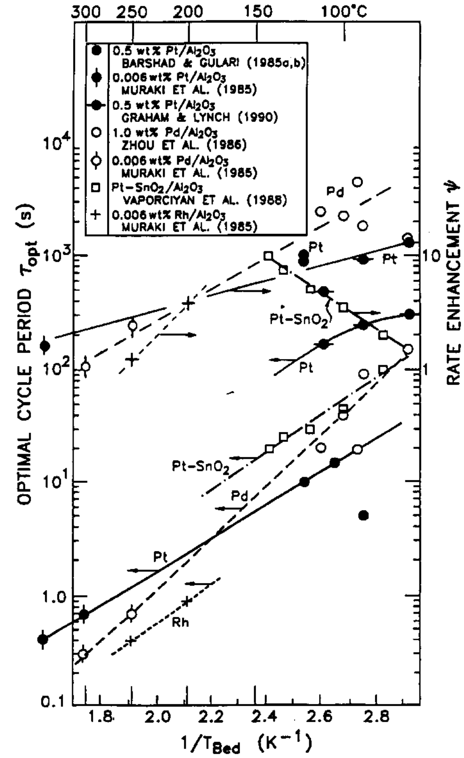

Fig. 7. Dependence of optimal cycle period and enhancement under CO–O_2 modulation of the rate of CO oxidation on the reactor temperature (Adapted from Silveston [19] with permission of the author).

lyst. Raising the time-average CO concentration in the feed from 0.665 vol.-% to 2.66 vol.-% increases the conversion enhancement caused by modulation. The stoichiometric number, bed temperature and space velocity were 1.0, 300°C and 30000 h^{-1} for this experiment.

The literature contains a number of studies which provide an interpretation of these observations, e.g. [13,26,27]. Muraki et al. [5] observed that CO reacts rapidly with adsorbed oxygen on switching reactants to the catalyst bed, but they found an induction time when oxygen was reintroduced. This time depended strongly on catalyst temperature and fell to less than 1 s as the temperature approached 200°C. These results indicate CO inhibition of the oxidation reaction at 200–300°C for the noble metal catalysts. Composition modulation increases O_2 adsorption by periodically decreasing CO coverage of the metal surface. Adsorption measurements on clean metal surfaces and low temperature show that the amount of CO adsorbed is up to 2 times the amount of O_2 adsorbed, whereas at 400°C CO adsorption is reduced sufficiently that the amount of oxygen adsorbed becomes larger than the amounts of CO. When the adsorbed population of O_2 matches the CO population, the oxidation rate reaches a maximum. Periodic composition forcing in this situation reduces the adsorbed amounts of CO and O_2 thereby suppressing the oxidation rate.

The importance of CO inhibition on the kinetics of CO oxidation on the noble metals indicates that oxidation is controlled by the reaction between adsorbed species and suggests these species should respond rapidly to gas phase fluctuations if concentration forcing at about 1 Hz effects rate and CO conversion. These conclusions were tested by Oh and Hegedus [28] using a wafer made of 1 wt.-% Pt/Al_2O_3 powder mounted in an IR transmission cell heated to 450°C. Oh and Hegedus employed the 2070 cm^{-1} line, corresponding to stretching of linearly adsorbed CO. From step-change forcing, they found that linearly adsorbed CO closely tracks the gas phase modulation. Oh and Hegedus comment that adsorption/desorption is rapid enough that equilibrium can be assumed at 450°C.

An explanation for the increase in the CO oxidation rate for the noble metal catalysts under composition modulation is oxygen storage on the catalyst surface. This occurs at the expense of CO adsorption which under steady state swamps the surface. As a result, time-average CO and O adatom concentrations are in better balance. Mathematical models incorporating storage and competitive adsorption [27,29–32] agree well with experimental data providing strong evidence for better adsorbate distribution as the source of improvement under forcing. However, simple models incorporating storage and adsorption do not predict CO conversions under composition modulation which exceed the maximum conversion under steady state at the same temperature and space velocity [33]. Yet, CO conversions greater than the maximum under steady state have been reported [22,24].

With catalysts where CO conversions exceed the maximum attainable under steady-state operation, Gulari et al. [22] suggest that the spatial distribution of adatoms on the catalyst surface increases under composition modulation. They suggest that adsorbate species are segregated into domains or ‘islands’ and that composition cycling decreases the size of the domains. Small adsorbent ‘islands’ in place of large ones would result in larger peripheries where reaction can occur and therefore in higher CO oxidation rates. Global enhancements of oxidation rates observed with Pd catalysts [22,24] suggests that only modulation can provide small ‘islands’.

CO and O_2 adsorption account for the temperature effects seen in Fig. 7. These are activated processes on noble metals above 200°C. Rates must therefore increase with increasing temperature. Consequently, if modulation is to enhance oxidation rates, cycling frequencies must also increase with temperature. Fig. 7 shows that the optimal cycling frequency indeed increases with temperature.

CO adsorption no longer dominates in the presence of both CO and O_2 at temperatures approaching 400°C. Thus, as catalyst temperatures rise, modulation becomes less effective in balancing CO and O adsorbate concentrations on the catalyst surface and higher cycling frequencies are necessary if modulation is not to unbalance the time-average adsorbate concentrations. Increasing temperature would be expected then to decrease the maximum rate enhancement under modulation just as the data in Fig. 7 demonstrate.

Particle size could also be a source of the differences observed. Fine catalyst particles generally were employed for low temperature modulation studies, while catalytic converter experiments were usually carried out with coarser particles. The role of intraparticle diffusion in CO oxidation on Pt/Al_2O_3 under composition modulation has been investigated theoretically by Cho et al. [30] using a single catalyst pellet model and later by Cho and West [34] experimentally. Although we will show that particle size is probably not the primary reason for differences found for CO oxidation over the individual noble metals and in catalytic converters, the Cho work explains why composition modulation does not always improve performance. It deserves, therefore, a detailed discussion.

For his model Cho assumed an isothermal particle with competitive adsorption, dissociative for O_2 and molecular for CO, and reaction between the adsorbed species. Model variables were normalized. Normalizing time in the model provides important insights as different choices lead to different characteristic times. If the cycle period is used, the characteristic time is the reciprocal of the modulation frequency. Other choices could be $1/S_t k$, the response time for the surface reaction; or, $\epsilon_p R^2/D_{\mathrm{eff}})_i$, the response time for intra particle diffusion of a reactant; or the space time, $\epsilon_B V/Q$. Cho observed that for typical operating conditions in catalytic converters: $\tau = 1$ s, the space time $= 10^{-3}$ s, the response time for reaction $= 10^{-2}$ s and the response time for diffusion $= 1$ s. The large period-to-space time ratio means that the gas composition surrounding the particle follows the feed fluctuations closely. However, since the period is about the same as the response time for diffusion, a significant influence of intraparticle diffusion on performance under cycling would be expected. This expectation was borne out by modelling and experimental results.

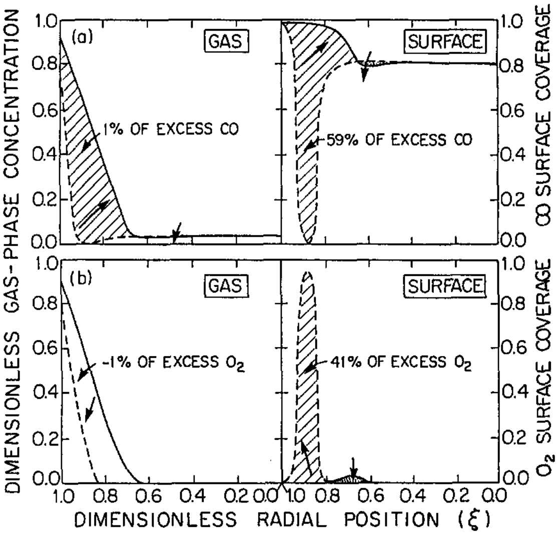

Fig. 8. Simulated storage and consumption of (a) CO and (b) O_2 during composition forcing (Reprinted from Cho [31] with permission of the American Chemical Society, the copyright holder).

Steady-state solution of the model showed that the Pt surface was largely saturated with CO at the temperatures and pressures assumed. Solution with sine-wave forcing of both CO and O_2 indicated that at times in a cycle there was much more oxygen stored on the catalyst surface so that CO conversion should be higher. Phase lag (ϕ) between CO and O_2 forcing was important for a catalyst particle with uniform radial Pt distribution. CO conversion was twice that calculated at steady state when $\phi = 180°$, which is the lag found in catalytic converters. Zero phase-lag forcing, where CO reaches a maximum in the feed concurrently with O_2, is still much better than steady state; indeed, conversion is only about 7% less than the 180° lag mode.

Under periodic operation (with $\phi = 180°$) not all the CO diffusing into the catalyst can be consumed by adsorbed O_2 and likewise for O_2 diffusion in the opposite half-cycle. Some of the CO (or O_2) must be stored. The storage at the end of the rich (CO excess) and lean (O_2 excess) half-cycles can be seen in Fig. 8. Most of the storage occurs on the Pt surface between $0.95 < \xi < 0.65$

where ξ is the dimensionless radial position. Further within the particle, some of the CO stored earlier in the rich half-cycle is given off by the surface ($0.65 < \xi < 0.45$). The centre of the particles ($\xi < 0.45$) is unaffected by cycling. A similar situation can be seen for O_2 in the bottom half of the figure. Cycling has no effect on adsorbed O_2 for $\xi < 0.6$; indeed there is no adsorbed O_2. The striking conclusion from Fig. 8 is that the cycling effects are constrained to the outer portion of the catalyst ($\xi > 0.4$ for CO and $\xi > 0.6$ for O_2). Cho et al. [30] examined the behaviour of band or egg-shell impregnated catalysts and noted that conversion under composition forcing was up to twice the conversion obtained for catalysts with uniform radial distribution of the active metal.

If at equal gas phase concentrations the adsorption of one reactant is favoured, chromatographic displacement can occur under composition modulation and leads to adsorption of the favoured reactant on the outer part of the pellet and adsorption of the least favoured at the pellet centre if any significant adsorption occurs at all. Periodic forcing of composition results in a large increase of reaction rate because it provides access of the less favoured reactant to the catalyst surface. On the other hand, if concentrations are adjusted so that adsorption between reactants is balanced, composition forcing causes imbalance and suppresses the reaction rate. From these considerations, Cho reasoned, and demonstrated by simulation, that forcing increases CO conversion for $SN < 1.2$ and for $SN > 5$ (O_2 adsorption dominates), whereas in between these regions steady state is the best mode of operation.

Some of the consequences of the simulation discussed above were examined experimentally. Cho and West [34] worked with 0.1 wt.-% Pt on low density, high surface area γ-Al_2O_3, impregnated to different depths and by different methods so as to have Pt dispersions from 50 to 100%. The feed stream was cycled at 0.5 Hz between a 'lean' stream consisting of 0.4 vol.-% O_2 and 0.2 vol.-% CO and a 'rich' stream with 0.2 vol.-% O_2 and 1 vol.-% CO. A 200–550°C temperature range was explored.

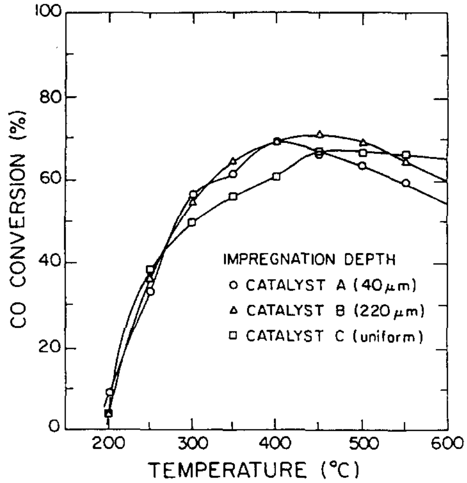

Fig. 9. Influence of Pt impregnation depth and dispersion for CO oxidation under periodic operation for a 0.1 wt % Pt/Al_2O_3 catalyst as a function of temperature (Reprinted from Cho and West [34] with permission of the American Chemical Society, the copyright holder).

With steady-state operation, 'shell' impregnation was found to be advantageous only at intermediate temperatures. At temperatures below 300°C, CO oxidation over the Pt catalyst is kinetically controlled whereas above 450°C the oxidation is controlled by mass transfer to the catalyst particle. Depth of impregnation is inconsequential in both these cases. Under periodic operation, however, the effect of impregnation depth is complicated. This is indicated in Fig. 9. Below 300°C, neither impregnation or dispersion affects CO conversion (catalyst 'A' has half the Pt dispersion of catalysts 'B' and 'C'). A 'shell' impregnation is useful between 300 and 450°C, but at higher temperatures a uniformly impregnated catalyst performs better. Maximum conversion at an intermediate temperature was explained by Cho and West [34] as the result of the growing desorption rate of reactants from the catalyst surface as temperatures increase. Cho and West argue that reactant storage on the catalyst surface causes CO oxidation rates to be higher under periodic than under steady-state operation. As a consequence of this argument, diffusional resistance for desorption will be more important for the uniformly impregnated than for the 'shell' impregnated catalysts. Adsorbate coverage by the reactants will be greater and therefore CO oxidation rates should be higher when uniform impregnation is used. Fig. 9 shows uniformly impregnated catalysts perform better than shell impregnated catalysts as catalyst temperatures approaches 600°C.

In further experiments with the uniformly impregnated catalyst, the time-average SN was fixed at 0.5, 1 and 2 and CO conversions under steady state and modulation at 0.5 Hz were compared. Under reducing conditions, steady-state operation offers higher CO conversion above 250°C. Cho and West (34) explain this result by weaker CO adsorption so that CO and O_2 achieve a more even balance on the surface. Composition modulation improves the O_2 coverage only slightly, so this benefit is outweighed by lower reactant levels in the alternating reducing and oxidizing portions of a cycle. Above 350°C however, sorption equilibria reduces O_2 surface coverage, but this reduction is less in periodic operation because of diffusional resistances and modulation at 0.5 Hz provides higher conversions than steady state.

The temperature behaviour with a stoichiometric CO and O_2 mixture was found to be quite different. Below 300°C, periodic forcing produces substantially higher CO conversion than under steady state. This occurs because modulation provides a better distribution of CO and oxygen adsorbate on the Pt surface. Increasing temperature brings the CO and oxygen adatom concentrations closer to stoichiometric so the advantage due to periodic changes to feeds richer in oxygen is lost. At high temperatures, bang–bang CO–O_2 modulation (switching between CO and O_2 feeds) used by Cho and West approaches a quasi-steady-state limit which has a very low conversion because equilibrium is now established instantaneously. Steady-state operation at SN = 1 and high temperature was found to be much better than modulation even at 0.5 Hz.

Under oxidizing conditions, the arguments advanced for SN = 1 still apply, so below 300°C modulation provides higher CO conversion than steady-state operation. At higher temperatures, conversion was complete for both operations so a comparison is no longer possible. Cho and West [34] extract further information from their experiments by calculating the excess CO oxidation for composition modulation versus stoichiometric, steady-state operation. From this, they conclude that the Pt surface is fully utilized below 300°C so the advantage of modulation is to increase the ratio of the oxygen to CO adatoms. Surface concentrations of oxygen and CO are sharply reduced above 400°C so that either oxygen or CO availability is rate-governing. Composition forcing should not have any benefit. The high temperature results of Cho and West are in substantial agreement with the effect of the A/F ratio in Fig. 4.

The important theoretical and experimental work of Cho [31] and Cho and West [34] indicates that diffusion is an important consideration in CO–O_2 modulation below 250 to 300°C. At higher temperatures, CO inhibition is less important so the benefits of modulation are limited or even disappear. Intraparticle diffusion continues to influence the oxidation rate, but it is not important with respect to the effect of composition modulation on performance. Temperature rather than catalyst particle size appears to be the important factor for the experimental differences observed. Before we turn to interference from the other reactions occurring on the three-way catalysts as an explanation of the differences, we will examine the effect of composition forcing on these reactions.

4. Studies of hydrocarbon oxidation under composition modulation

Propylene and propane combustion under forcing of the A/F ratio are discussed by Shinjoh et al. [35]. The platinum (Pt) and palladium (Pd) catalysts used contained 0.05 g/l of catalyst or were 0.006 wt.-% metal, while the rhodium (Rh) catalyst contained 2.0 g/l. Space velocity was 30000 h^{-1}. Temperature and cycle period were the independent variables; feed compositions were switched between 0.01 and 0.4 vol.-% hydrocarbon and 0.1 and 2.0 vol.-% O_2. These

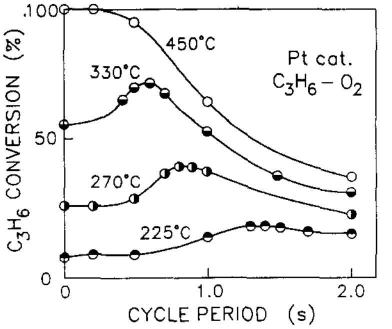

Fig. 10. Propylene conversion as a function of cycle period at different temperatures for a Pt catalyst and SV = 30,000 h^{-1} (Reprinted from Shinjoh et al. [35] with permission of Elsevier Science Publishers B.V., the copyright holder).

typify rich and lean fuel mixtures. Cycles were symmetrical ($s = 0.5$).

Composition forcing increased conversion at the lower temperatures for the Pt and Rh catalysts, but there was no improvement for Pd. Fig. 10 shows only Pt data as a plot of time-average conversion vs. cycle period for different temperatures. Steady-state data for the time-average feed composition is given by the point at $\tau = 0$. Combustion enhancement under composition forcing are smaller than those observed for CO oxidation (Fig. 6) at about the same temperature. Just as for CO oxidation, increasing the temperature decreases the enhancement achieved through A/F cycling and also decreases the modulation frequency that maximizes hydrocarbon combustion. Measurements for propane oxidation, given by Shinjoh et al. for the Pt catalyst, are similar to the propylene results except that conversions are lower by a factor of 2-to-3-fold.

Examination of reactant transients after a composition switch show a relatively slow rise in O_2 after a switch to an O_2-rich feed, whereas O_2 disappears from the outlet instantaneously after a propylene-rich feed is introduced. Kinetic measurements indicate a negative reaction order in propylene for Pt and Pd catalysts, while the order is positive for oxygen. This suggests that the hydrocarbon or its partially oxygenated intermediate are more strongly adsorbed on the metal than oxygen. The orders are reversed for rhodium. Shinjoh et al. [35] conclude that under steady-state operation the noble metal catalysts are reactant inhibited so that the mechanism for the improvement through A/F modulation appears to be balancing the adsorbate concentrations on the surface. In an earlier paper, Shinjoh et al. [8] observe that whenever the product of the reaction orders is negative, composition forcing activates the noble metal catalyst provided an optimum or near-optimum cycling frequency is chosen.

5. Studies of NO reduction under composition modulation

NO reduction by CO was investigated by Muraki and Fujitani [36] for the same three catalysts used by Muraki et al. [3] for CO oxidation. For several cycling experiments a Pd loading of 0.24 wt.-% was used and this loading was also chosen for the temperature-programmed desorption (TPD) experiments which supported the study. Nitric oxide (NO) was assumed to represent the mixture of oxides present in automotive exhaust. In most experiments, symmetrical switching ($s = 0.5$) between NO and CO was used with each at 0.3 vol.-% when present in the reactor feed. The diluent was He.

Fig. 11 compares the conversion of NO at 400°C and SN = 1 for different cycle periods. SN is defined for the NO–CO system as NO (vol.-%)/CO (vol.-%). The data points at zero seconds represent steady-state. Clearly, modulation leads to an enormous increase in NO conversion for the

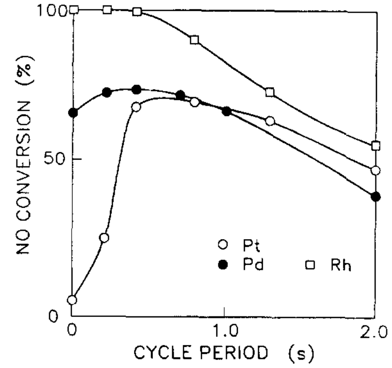

Fig. 11. Comparison of NO conversion on noble metal catalysts at 400 C, SN = 1, SV = 30,000 h^{-1} for switching between 0.3 vol.% NO and 0.3 vol.% CO (Adapted from Muraki and Fujitani [36] with permission of the American Chemical Society, the copyright holder).

Pt catalyst. Pd is also activated by forcing, but the conversion improvement is less dramatic. Rhodium (Rh) is an effective low-temperature catalysts for NO_x reduction, so it is not surprising that the figure shows no improvement under modulation. Probably the high steady-state conversion makes improvement difficult to detect and forcing frequencies greater then the 5 Hz used by the Toyota researchers may be necessary to provide a conversion increase.

Effect of temperature and stoichiometric number on conversion under forcing are discussed by Muraki and Fujitani [36] for the Pt catalyst. With cycling between feeds containing just one of the reactants, there was a dramatic increase in conversion, just as observed for CO oxidation. An optimal cycling frequency was also observed as in Fig. 10. Regardless of the time-average SN, increasing temperature increased this optimal frequency. These frequencies appear to be higher for oxidizing mixtures and may be about 5 Hz for SN = 1.5 at 450°C. With a reducing mixture, SN = 0.25, the optimum frequency falls to 1 Hz.

Reducing NO with CO forms either N_2O or N_2. Nitrogen formation dominates, but appreciable amounts of N_2O appear when the reactor feed is oxidizing. The nitrous oxide side reaction proceeds at temperatures as low as 300°C for the Pt and Pd catalysts at steady state. It is important up to 500°C if the mixture is non-stoichiometric [6]. Bang–bang composition forcing, switching between feeds containing just one of the reactants, substantially reduced N_2O formation. Indeed at SN = 1 and 400°C, selectivity to nitrous oxide drops from 0.6 at steady state to less then 0.2 for a cycle period of 0.5 seconds. The formation rate of N_2O reaches its lowest level when NO conversion is at its highest level.

Kinetic and temperature programmed desorption (TPD) measurements on the Pt, Pd and Rh catalysts undertaken to interpret the modulation experiments [6,7,36] found negative orders of reaction for CO with the Pt and Pd catalysts, whereas the reduction was first order in NO. CO inhibition of the reduction seems probable. TPD measurements for these two catalysts indicated dissociative NO adsorption on weakly bonding sites, whereas CO adsorbs on both strongly and weakly bonding sites. CO_2 desorbs from the strong sites suggesting disproportionation of CO may be occurring. With the Rh catalyst, reduction is about zero order in CO while the order is slightly negative for NO. CO adsorption on weakly bonded sites is greater than for Pt or Pd while CO_2 adsorbed on the strong sites is less. Muraki and Fujitani [36] conclude that Rh is a good catalyst under steady-state operation because CO inhibition is less significant. The positive effect of CO–NO switching on conversion over Pt and Pd catalysts was attributed to scavenging of adsorbed CO from the catalyst surface during NO exposure which increased NO adsorption. Scavenging of adsorbed atomic oxygen during the CO portion of the cycle resulted in CO_2 formation. Nitrogen was observed mainly when the feed contained NO [6,7]. Pulse experiments also suggested that N_2O and N_2 form on different sites. NO adsorption on a surface rich in adsorbed oxygen favours N_2O, while on a surface depleted of atomic oxygen, N_2 is the predominant product. Muraki and Fujitani explain the improved selectivity to N_2 with CO–NO bang–bang switching by the exposure of NO to a surface largely free of atomic oxygen when the reactant in the feed changes from CO to NO. Increased conversion arises because composition forcing decreases the time-average concentration of CO on the Pt and Pd surfaces, while raising the time-average NO concentration. The improved balance of the adatom species results in higher reduction rates.

6. Studies of competing reactions under A/F modulation

The competing CO–HC oxidation reactions were investigated by Muraki et al. [6] under a modulation policy consisting of periodically and symmetrically stepping up either the CO or the O_2 vol.-% in the reactor feed. Periods from 0.2 to 2 s were used, time-average feed composition was 1.33 vol.-% CO, 0.77% O_2, and 0.0233% C_3 (a

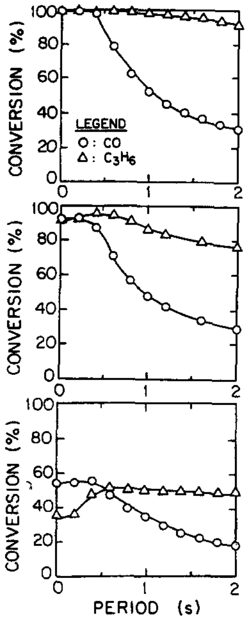

Fig. 12. Effect of cycle period on conversion at 400°C with CO-O_2 modulation for CO (o) and C_3 (Δ): (top) Rh, (middle) Pd, (bottom) Pt catalysts. Steady state is $\tau = 0$ (Adapted from Muraki et al. [6] with permission of Nippon Kagaku Kaishi, the copyright holder).

stoichiometric mixture), temperatures were 280 and 400°C and the space velocity was 30000 h^{-1}(STP). The investigators used Pt, Pd and Rh supported on α-Al_2O_3 at a metal loading of 0.05 mg/ml. The low loading simulated the CO adsorption capacity of aged commercial automotive exhaust catalyst.

At 400°C and the relatively low SV, conversions were high for the Rh and Pd catalysts, but just moderate for Pt under both steady state and cycling as Fig. 12 shows. Steady state is represented in the figure by the data point at $\tau = 0$. At high conversions, composition modulation has only a small effect because improvements are difficult to measure when conversion is close to 100%. Thus, in Fig. 12 (middle part) modulation at about 2 Hz increases C_3 conversion slightly for the Pd catalyst. No improvement can be seen for the Rh catalyst. With the Pt catalyst, a small increase in conversion can be seen in Fig. 12 (bottom part) for CO at 2 Hz, but there is a large increase in conversion through cycling for C_3 with periods greater than 0.5 s.

Only the Pd formulation was investigated at 280°C: Muraki et al. [6] observed a large increase in C_3 conversion at 2 Hz, but the steady-state conversion at this temperature had dropped to 55%. Modulation also increased CO conversion by about 10% at 2 Hz, but conversion dropped off rapidly as the frequency decreased. Muraki et al. [6] comment that the frequency which maximizes conversion decreases when changing from a single-reaction system to one with two reactions. Asymmetrical forcing experiments showed higher conversions only when the high-O_2 exposure was extended. From these results, it is evident that oxidation rates over the noble metal catalysts are CO-and hydrocarbon-inhibited. Modulation improves performance by increasing O_2 access to the catalyst surface.

The NO–CO–O_2 system has been examined by several investigators, mainly because it was thought to be a model set of reactions for TWCs. Hegedus et al. [9] worked with a Pt/Al_2O_3 catalyst (1 wt.-% Pt) in an integral reactor and in an IR transmission cell with the catalyst in wafer form. With the latter, the response of a CO–Pt stretching band, corresponding to linearly adsorbed CO, and an isocyanate band to a periodically changing gas phase composition was observed. Isocyanate is thought to be an intermediate in NO reduction by CO. Measurements were made at about 510°C with the feed oscillating between an SN of 0.58 and 1.42. Fig. 13 shows the response of the CO band in (a) to a 2 s and 6 min cycle period and, in (b), the effect of switching time ($= \tau/2$) on the response amplitude. In slow cycling, the CO–Pt band (the only one observed at 510°C) follows the square wave input closely, but the response becomes sinusoidal in fast cycling with a small diminution of amplitude. Indeed, (b) shows the amplitude decreases sharply only near a frequency of 0.5 Hz. The isocyanate surface species, Fig. 14, is unable to follow the gas phase in slow cycling. This amplitude vs. switching time plot shows the signal becomes constant at a switching frequency of 1 Hz. Furthermore, the time-average surface concentrations decrease with switching time. The integral reactor

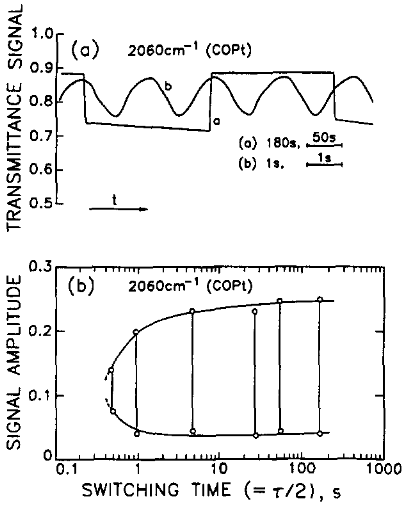

Fig. 13. Transmission IR response of an adsorbed CO species at 2060 cm^{-1} to modulation of O_2 concentration for a 0.1 wt % Pt/γ-Al_2O_3 catalyst at 510°C: (a) time variation of transmittance at $\tau = 2$ s and 360 s, (b) amplitude of transmittance variation as a function of switching time ($\tau/2$) (Adapted from Hegedus et al. [9] with permission of the American Chemical Society, the copyright holder).

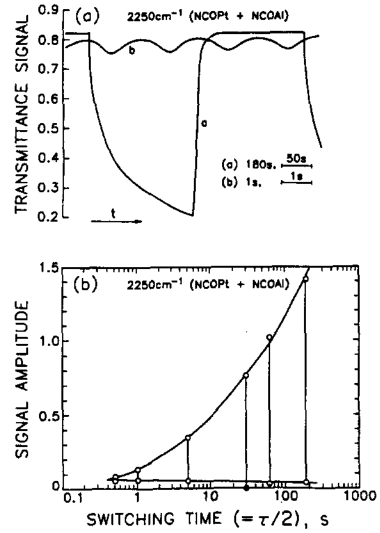

Fig. 14. Transmission IR response of an adsorbed isocyanate species at 2250 cm^{-1} to modulation of O_2 concentration for a 0.1 wt % Pt/γ-Al_2O_3 catalyst at 510°C: (a) time variation of transmittance at $\tau = 2$ s and 360 s, (b) amplitude of transmittance variation as a function of switching time ($\tau/2$) (Adapted from Hegedus et al. [9] with permission of the American Chemical Society, the copyright holder).

experiment, carried out at a mean bed temperature of 525°C and a SV of 104000 h^{-1}(STP) showed conversion increasing as switching time decreased. Again, CO and perhaps isocyanate inhibit the oxidation–reduction reaction. Adsorbed CO responds to gas phase composition fluctuations, but isocyanate, an intermediate, does not, so the behaviour of the TWC for the CO–NO–O_2 reactions seems to be governed by surface processes.

Muraki et al. [6] used their catalysts and reactor system, discussed above, for the NO–CO–O_2 reaction system, but made measurements only at 400°C. Although steady-state conversions are absent, Fig. 15 suggests that cycling does not increase CO or NO conversion for the Rh and Pd catalysts. Conversions, however, are between 80 and 100% at the experimental conditions used. There is a 15% increase in NO conversion and just under a 10% increase for CO for the Pt catalyst at 3–4 Hz. These results agree with the investigation of Hegedus et al. [9] and identify a strong effect of modulation frequency on performance. In addition they show that A/F cycling can improve performance if the frequency is high enough. Comparison with Fig. 11 suggests the presence of the CO–O_2 reaction has not changed the NO–CO behaviour under cycling significantly.

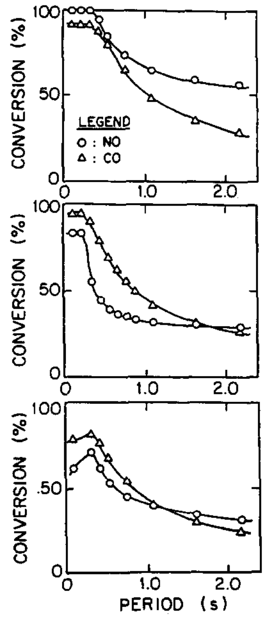

Fig. 15. Effect of cycle period on conversion at 400°C with CO and O_2 modulation for NO (o) and CO (Δ): (top) Rh, (middle) Pd, (bottom) Pt catalysts. Steady state is $\tau = 0$ (Adapted from Muraki et al. [6] with permission of Nippon Kagaku Kaishi, the copyright holder).

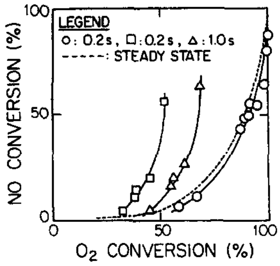

Fig. 16. Effect of cycle period on the partitioning of CO between the NO and O_2 reduction reactions at SN = 1 over a 0.006 wt % Pd/α-Al_2O_3 catalyst in an integral reactor at 400°C with CO-O_2 modulation. Steady-state partitioning given by the dashed curve (—) (Adapted from Muraki et al. [4] with permission of Nippon Kagaku Kaishi, the copyright holder).

The Pd/γ-Al_2O_3 catalyst used in the above experiments was singled out for detailed study at different SN by Muraki et al. [4]. Symmetrical modulation of both the CO and O_2 concentrations continued to be used and the temperature was maintained at 400°C. Modulation had a large effect (up to 100%) on NO conversion and could increase conversion except at or near the stoichiometric mixture if the proper cycle period was chosen. The optimum cycle period for NO conversion depended on the SN. With respect to CO, modulation affected conversion, but increased it above steady-state conversion only under strongly reducing conditions. At higher stoichiometric numbers, steady-state operation was substantially better than composition modulation.

Partitioning of CO between the O_2 and NO reactions depends on the stoichiometric number. Muraki et al. [4] show that CO oxidation by O_2 is favoured under steady-state operation and this preference is strongest at higher CO concentrations (low SN). Fig. 16 shows that CO–O_2 modulation shifts the partitioning towards NO reduction sharply and this shift is frequency-dependent. At the highest frequency used, 5 Hz, the partitioning is essentially identical to that obeyed at steady state. This is consistent with the observations of Hegedus et al. [9] that the formation of the isocyanate intermediate in NO reduction is slow relative to CO oxidation and that this intermediate cannot follow fast composition fluctuations. Cycle period influences the kinetics of the two reactions as well. Under fast cycling (5 Hz) the effect of O_2 partial pressure on the CO oxidation rate and the order of the reaction with respect to oxygen is the same as at steady state. Increasing the cycle period decreases the rate of the CO–O_2 reaction and eliminates the zero order dependence on O_2 partial pressure at O_2 pressure above 0.007 bar. At steady state and up to $\tau = 0.2$ s, the NO reduction rate decreases dramatically for $P_{O_2} > 0.01$ bar. With CO–O_2 modulation at 1 Hz, increasing oxygen partial pressure decreases the NO reduction rate, but at $P_{O_2} = 0.018$ bar, the reduction rate is almost 15 times the steady-state rate. Muraki et al. [4] conclude that under steady-state operation CO inhibits NO reduction. Modulation of the A/F ratio suppresses the inhibition and thereby promotes NO reduction.

The studies summarized above show that modulation continues to affect performance when competing reactions are occurring on the catalyst surface. They do not indicate, however, that there is significant interference between the reactions under forcing of the A/F ratio.

7. Studies on actual and simulated automotive exhaust

The Toyota research team included experiments employing actual and synthetic automotive exhaust in their extensive study of CO–O_2 modulation of TWCs. The results of Muraki et al. [6] for a temperature of 400°C and a time average SN = 1 are plotted in Fig. 17 for the catalysts, experimental system and procedures employed in the studies discussed in previous sections. Conversions are shown as a function of cycle period for NO, CO, HC and O_2. Steady-state conversions are not given, but can be estimated from the trend of the data. Modulation increases conversion of all reactants only for the Pt catalyst. With the exception of NO reduction over Pd and hydrocarbon oxidation over Rh, which increase, modulation suppresses conversion for the Pd and Rh catalysts. Conversion increases for the Pt catalyst can be sizeable: for C_3 oxidation and NO reduction they are about 100%. The optimal frequencies,

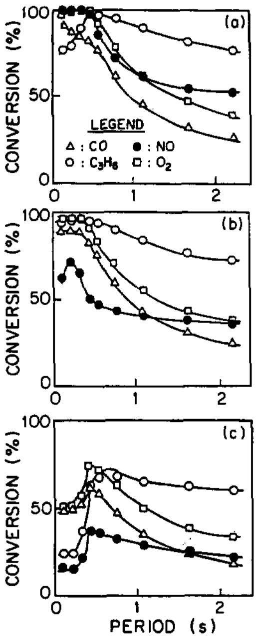

Fig. 17. Effect of cycle period on NO, HC, CO and O_2 conversion over Rh, Pd, Pt catalysts supported on α-Al_2O_3 in an integral reactor at 400°C with CO- O_2 modulation: (a) Rh, (b) Pd, (c) Pt (Adapted from Muraki et al. [6] with permission of Nippon Kagaku Kaishi, the copyright holder).

according to the figure, are about 2 Hz. These are about the same as the optimal frequencies found for the CO–C_3–O_2 system, but they are lower than those for the NO–CO–O_2 system.

Muraki et al. [5] examined the effect of amplitude and cycle period on HC, CO and NO conversion over the noble metal catalysts at 400°C. Forcing the A/F ratio for amplitudes from 0.3 to 1.2 and for frequencies from 0.3 to 4.5 Hz, these investigators found that composition modulation was beneficial for the Pt catalyst for NO and HC conversion between 0.5 and 3 Hz, while it marginally increased CO conversion in a narrow frequency band at or above 2 Hz. For the Pd catalyst modulation between 1 and 3 Hz marginally improved NO and HC conversions, while matching the nearly 90% CO conversion achieved under steady state. With the Rh catalyst, modulation provided no improvement, however it matched the nearly complete conversion at steady state when the cycle frequency exceeded 2 Hz. These conversions are in good agreement with later studies by Muraki et al. [6]. The earlier work by Muraki et al. [5] found that for HC conversion over the Pt catalyst and NO conversion over the Pd catalyst the frequency band which improves conversion becomes a function of the forcing amplitude. Increasing amplitude, in general, reduces conversions of all the reactants with just a few exceptions. These are NO reduction over Pt where conversion diminishes only if the amplitude of the A/F ratio exceeds 0.8, NO reduction over Pd where amplitude has just a small but varying effect on conversion, and HC conversion where amplitude does not affect conversion. Apart from Pt, the amplitude effect on conversion disappears at the highest frequencies used.

Schlatter et al. [17] investigated the effect of catalyst aging through exposure to the exhaust. Periodic and steady-state operations were about equally affected at SN = 1. However, Schlatter et al. observe that modulation no longer increases conversions away from the stoichiometric A/F ratio when aged catalysts are used. Yokota et al. [18] used aged catalysts in their measurements of the effect of A/F modulation on conversion. An actual automotive exhaust was employed. Catalysts tested were the same as those used by Muraki et al. [5], except that the Pt loading was increased to 0.5 mg/ml to compensate for the lower activity of that catalyst. Experiments were performed with converter inlet temperatures between 340 and 360°C.

Fig. 18 compares NO_x, total hydrocarbon and CO conversions under A/F modulation at 1 Hz and amplitudes from 0.3 to 1.2 in the A/F ratio with the steady-state conversions ($\pm$A/F = 0). At the stoichiometric A/F ratio modulation depresses conversions for Rh and Pd, except for NO reduction on Pd, whereas modulation raises conversions for the Pt catalyst. These observations are consistent with those reported by Muraki et al. [5,6]. There is agreement also with GM research [9–11,17,34,37] which showed no conversion amelioration for TWCs at a stoichiometric A/F ratio by modulating the A/F ratio.

On the other hand, Fig. 18 suggests that under modulation a Pt or Pd catalyst performs as well as Rh at A/F ratios off the stoichiometric. Different

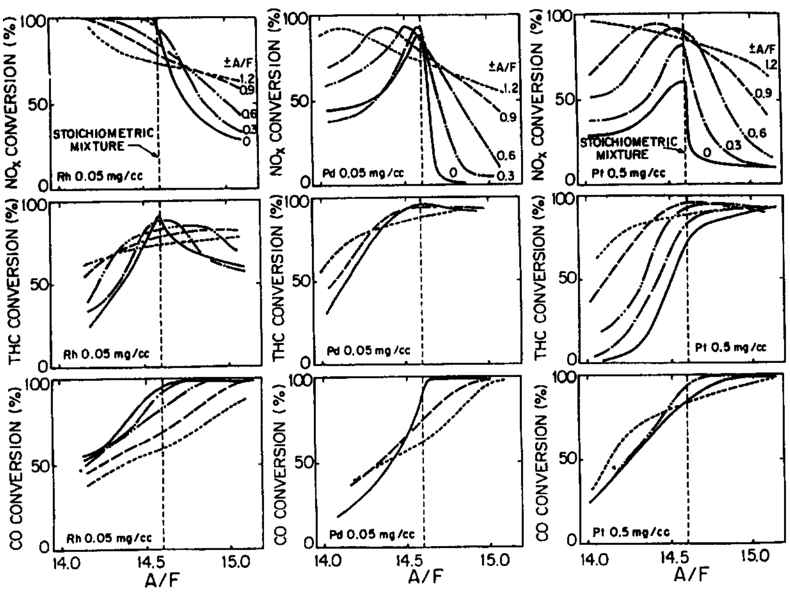

Fig. 18. NO, HC and CO conversion as a function of the time-average A/F ratio and cycle amplitude over Rh, Pd, Pt catalysts supported on α-Al_2O_3 in an integral reactor using an automotive exhaust with modulation of the A/F ratio at 1 Hz: (left) Rh, (middle) Pd, (right) Pt. Inlet temperature to the catalytic converter was 340-360°C (Adapted from Yokota et al. [18] with permission of the authors).

cycle periods and amplitudes were considered by Yokota et al. [18]. Fig. 18 shows conversions for the Rh catalyst are between 90 and 100% for NO_x, HC and CO. Steady-state conversions for Pd are close to those for Rh, except for NO reduction. This reaction, however, is stimulated by forcing so that at about 1 Hz NO conversion reaches 95%. With respect to Pt, steady-state performance is well below that exhibited by Rh. Modulation of the A/F ratio between 0.5 and 1.5 Hz brings the performance of this catalyst up to the Rh level, although only the 1 Hz data are shown in Fig. 18.

8. Does A/F modulation improve three-way catalyst performance?

Recapitulating our examination of the A/F modulation literature, it is well established that the unavoidable modulation of the A/F ratio affects conversions over TWCs. Unfortunately, the effect is not favourable for rhodium (Rh) and TWCs containing Rh. Modulation improves only NO_x reduction and then just slightly under TWC operating conditions. Toyota researchers, however, have demonstrated that large conversion enhancements are possible through modulation for Pt catalysts. This pattern is observed for CO oxidation, HC oxidation, NO_x reduction and when these reactions occur together. Even though beneficial effects have been found for Pt catalysts, they are about an order of magnitude less than those observed for CO oxidation over Pt under non-automotive conditions.

There are several explanations. First of all, increasing temperature sharply decreases the benefit of composition modulation. This is evident from Fig. 7 and is explained by the temperature dependence of CO and O_2 adsorption equilibria. The work of Cho [31] and Cho and West [34] indicate intraparticle diffusion reduces modulation enhancements above 300°C near SN = 1 even with egg-shell deposits of the noble metals. Perhaps the aging effect which reduces the enhancement through A/F modulation is a consequence of diffusional resistance and results from carbon deposition or pore size changes caused by temperature cycling. Catalytic converters normally operate between 400 and 600°C and the A/F control keeps the inlet to the converter close to SN = 1 regardless of motor operation. Consequently, the 10-fold enhancements observed for CO oxidation using Pt or Pd catalysts in powder form at temperatures below 150°C cannot be expected.

Our second explanation comes from the observation that conversion enhancement depends on frequency. Thus, at any temperature, there is a narrow band of modulation frequency which raises conversion above that attained under steady state for each reaction over all of the noble metals now used in TWCs. This is evident in Fig. 6, Fig. 10–12 and Fig. 17. The band can be represented by a single frequency called an optimal frequency. Fig. 7 demonstrates that optimal frequencies depend on temperature. Extrapolating data in Fig. 7 to 400°C indicates that the optimal frequencies will be about 3 Hz for Pt and about 10 Hz for Pd and Rh. The frequency of the fundamental A/F modulation caused by feedback control ranges between 0.5 and 2 Hz and so it is sub-optimal. Motor speed changes impose an irregular 10 Hz disturbance, but its amplitude is small. Local mixing in a packed bed would probably smooth out this disturbance, although it might persist in a monolith converter.

Other causes of the discrepancy between catalytic converter performance and the low temperature CO oxidation experiments are aging which reduces enhancement under modulation according to Schlatter et al. [17]. Interference through the competing reactions in the converter does not seem to be a source since interference seems to be very small. An experimental problem has been that the steady-state conversions are so high in catalytic converters that it is difficult to detect changes caused by A/F modulation.

Are there other considerations for catalytic converters besides NO_x, hydrocarbon and CO conversion in the region of a stoichiometric A/F ratio? Two are mentioned in the literature. The first is the operational window, i.e, the range of the A/F ratio for which the TWC is able to achieve conversions greater than 90%. Fig. 4 indicates this range is narrow, about 0.1 in terms of the A/F ratio.

A/F modulation at about 1 Hz benefits conversion away from the stoichiometric ratio. This is evident in Fig. 4 and 18 and was also shown by Cho and West [34]. Fig. 4 shows enhancements at $A/F \leq 14.6$ and ≥ 14.8. Conversions under modulation are only 50 to 60% compared to CO and NO conversions $\geq 90\%$ at the stoichiometric ratio. Thus, the data of Schlatter et al. [17] suggest the window has not been enlarged by modulation. The results of Yokota et al. [18], however, show an enlargement. In lean mixtures, $SN < 1$, Fig. 18 shows that modulation raises NO conversion well above that possible under steady-state operation. Increasing amplitude generally increases conversion. For the Pd and Pt catalysts, conversion increases through modulation even in rich mixtures ($SN > 1$). These enhancement occur within 0.1 A/F units from the stoichiometric ratio. With respect to hydrocarbon oxidation, modulation raises conversion in rich mixtures for all three catalysts. The improvements are substantial for the Rh and Pt catalysts. Finally, modulation of the A/F ratio increases CO conversion over the Pd and Pt catalysts at $SN > 1$ but the improvement is smaller than what was seen for NO reduction and HC oxidation. The modulation effects found by Yokota et al. for non-stoichiometric A/F ratios are considerably greater than those reported by Schlatter et al. [17] or by Taylor and Sinkevitch [37]. Measurements of the latter investigators were made at temperatures about 100°C to 150°C higher, used a smaller amplitude and employed a different catalyst. There is, thus, some evidence that involuntary modulation of the A/F ratio widens the operational window for catalytic converters.

The second consideration is light-off. The light-off temperature of a catalyst is defined as the temperature at which 50% conversion is achieved. Light off is an important consideration for urban driving because the converter may not reach its operating temperature before the trip is over. Lower light-off temperatures are desirable for TWCs. Studies of the effect of A/F modulation on light-off behaviour are scarce. Light-off data of Muraki et al. [5] for C_3H_6, CO and NO, measured by raising the reactor temperature at 2°C/min, are displayed as a function of forcing period in Fig. 19 for each of the three noble metal cata-

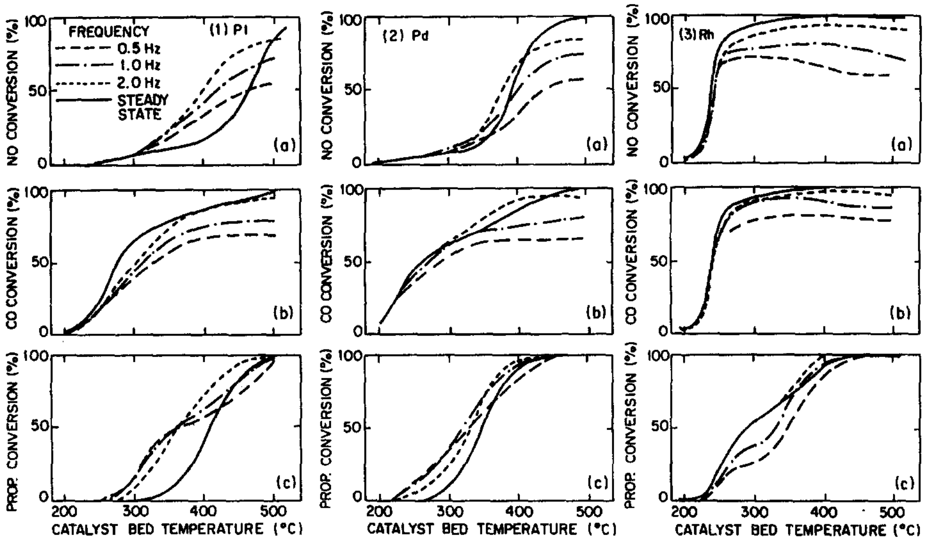

Fig. 19. NO, CO and HC conversion as a function of catalyst bed temperature and cycle frequency over Rh, Pd, Pt catalysts supported on α-Al_2O_3 in an integral reactor with CO and O_2 modulation at an amplitude of ± 0.5 A/F: (1) Pt, (2) Pd, (3) Rh (Adapted from Muraki et al. [5] with permission of the American Chemical Society, the copyright holders).

lysts. The A/F ratio amplitude was 0.5. Modulation decreases light-off temperature for NO reduction and C_3 oxidation for the Pt and Pd catalysts. The decrease is about 75°C for the former catalyst. Light-off temperature increases for CO oxidation for both of these catalysts, and for C_3 oxidation on the Rh catalyst. Modulation does not affect light-off on the Rh catalyst for NO reduction and CO oxidation. These results were obtained with fresh catalysts, although the metal loading was kept low so the adsorption capacities corresponded to those exhibited by used catalysts.

Taylor and Sinkevitch [37] also explored light-off behaviour for a synthetic automotive exhaust under composition modulation expressed in terms of the A/F ratio. Space velocity was 20000 h^{-1}(STP), temperature 550°C and the forcing frequency was 1 Hz. The cycling experiments were repeated at a forcing frequency of 0.1 Hz which is low compared with other studies of A/F modulation where conversion effects were noted. The catalyst was 0.68 wt.-% Pt, 0.031% Pd, 0.007% Rh and 2.68% Ce on a γ-Al_2O_3 and was aged by extended exposure to automotive exhaust. Results are given in Fig. 20. Light-off for CO oxidation seems unaffected by cycling, however propylene oxidation is affected. The temperature decrease for 50% conversion is about 50°C. The effect of cycling is sensitive to the A/F ratio for NO reduction. At SN = 1, light-off temperature increases by about 20°C under modulation, while for a lean mixture, light-off is not affected. These

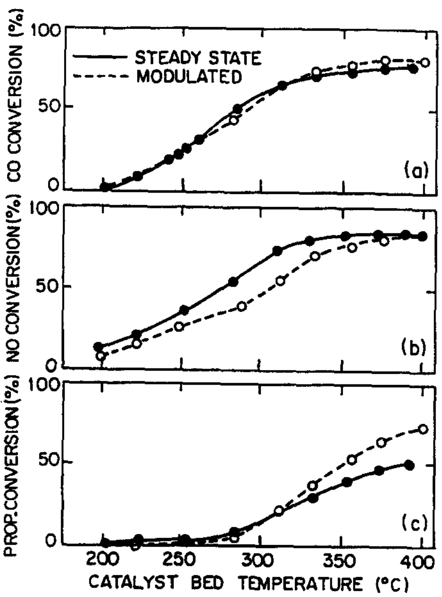

Fig. 20. CO, NO and C_3 conversion as a function of catalyst bed temperature for steady-state and periodic operation over a Pt/Pd/Rh/Ce/γ-Al_2O_3 catalyst in an integral reactor. A/F modulation at 1 Hz and an amplitude of ± 0.15 A/F (Adapted from Taylor and Sinkevitch [37] with permission of the American Chemical Society, the copyright holder).

results generally agree with the observations of Muraki et al. [5]. Muraki and Fujitani [36] experimented with NO reduction by CO on a supported Pt catalyst and found light-off was lowered by almost 150°C. Shinjoh et al. [35], however, studied C_3H_6 oxidation over three noble metal catalysts and observed no modulation effect on the light-off temperature. In summary, there is some evidence that A/F modulation decreases the light-off temperature for NO reduction and hydrocarbon oxidation for TWCs.

The final question is what might be done to benefit from A/F modulation. There are too few investigations in the literature to answer this question with respect to the operational window for converters or their light-off behaviour. A negative answer is possible for CO, NO_x and hydrocarbon conversion. Modulation at an optimal frequency might well enhance conversions. Modulation now forced by the sensor, feedback loop and the air flow damper would require a frequency increase to 5 to 10 Hz through redesign of the loop. Benefits of the higher frequency, unfortunately, would be small because mixing in the packed bed converters would reduce amplitude significantly. Benefits could be larger with the monolith design. Further study of this question is needed.

9. Nomenclature

A	Amplitude (various units)
A/F	Air/fuel ratio (as weight)
D_{eff}	Effective diffusivity (m^2/s)
k	Reaction rate or adsorption/desorption constant (various units)
HC	Hydrocarbon
P	Pressure (kPa)
Q	Volumetric flow-rate (m^3/s)
R	Pellet radius (mm)
S	Specific surface area (m^{-1})
SN	Stoichiometric number defined by Eqs. (1) and (2)
SV	Space velocity, usually STP. This is the ratio of the volumetric flow-rate to the catalyst volume (h − 1)
TWC	Three-way catalyst
t	Time (s). Mean residence time or space time (s)
V	Bed volume (m^3)

Greek

τ	Cycle period (s)
Ψ	Enhancement factor (time-average rate/steady-state rate)
Ψ^*	Global enhancement (time-average rate/maximum steady-state rate)
ϵ_B	Bed porosity
ϵ_p	Pellet porosity

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