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## Modeling and analysis of rapid catalyst aging cycles

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### ABSTRACT

The primary mode of deactivation of automotive emission control catalysts is thermal aging, and it is well-known that high-temperature lean aging conditions are particularly detrimental. Since evaluating the long-term durability of automotive catalysts is costly and time-consuming, rapid catalyst aging cycles have been developed to mimic (in a reduced time) the catalyst deactivation under real-world driving conditions. One of the commonly used rapid catalyst aging tests is an exothermal aging cycle, which involves a combination of fuel-rich engine operation and supplemental air injection to generate high-temperature lean conditions within the catalyst bed. In this work, we use the previously developed transient three-way catalyst model to investigate the time evolution of the axial temperature profiles and exhaust air–fuel ratio (A/F) along the catalyst bed during the course of the exothermal rapid aging cycles. We find that the thermal front propagates downstream through the catalyst bed relatively slowly (compared to the concentration front) and this can limit the location within the catalyst bed and duration for high-temperature lean exposure. We also investigate how variations of some of the key system design and operating parameters can affect the extent and duration of high-temperature lean exposure. Finally, a simple analytical expression is developed which allows one to estimate the time it takes for the thermal front to travel through the catalyst bed. This time can be compared with the period of the lean A/F operation during the aging cycle to determine the location and duration of high-temperature lean exposure.

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**Keywords:** Aging cycles; Rapid aging tests; Automotive emission control catalysts; Catalyst deactivation

### 1. Introduction

Catalyst deactivation, the irreversible loss of catalytic activity and/or selectivity over time, is a phenomenon of great importance in the practice of industrial catalytic processes including catalytic control of automobile exhaust emissions. Deactivation of automotive emission control catalysts can result primarily from poisoning and thermal degradation. Poisoning refers to the accumulation of engine oil-derived contaminants, such as P, Zn and Ca, on the catalyst surface, thereby blocking the access of the reactants to or catalytic reaction on the active sites (Beck et al., 1997a, b; Darr et al., 2000; Rokosz et al., 2001). Thermal degradation occurs as a result of exposure of the catalyst to high-temperature conditions (Barbier and Duprez, 1994; Bartholomew, 2001; Fiedorow et al., 1978; Stenbom et al., 1990). This causes sintering of the noble

metals as well as base metal oxide promoters, such as ceria, resulting in loss of the catalytic surface area and the promotion effect due to particle growth. It is widely accepted that the sintering of the noble metals due to high-temperature exposure is the major mode of the deactivation of three-way catalysts (Kašpar et al., 2003; Koltsakis and Stamatelos, 1997).

Unlike poisoning, thermal aging leads to catalyst deactivation throughout the converter (negatively impacting both light-off and warmed-up performance) since the sensible heat associated with the incoming gas as well as the reaction exotherm generated in the upstream section during the aging is carried downstream by the exhaust flow (Oh and Cavendish, 1982). One important feature of thermal aging is that its impact depends strongly on the gaseous atmosphere that the catalyst is exposed to during the aging. In reducing atmosphere,

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## Nomenclature

$a_j$	catalyst surface area per unit volume of the monolith, mol-site/m <sup>3</sup>
$A$	monolith frontal area, m <sup>2</sup>
$C_d$	cell density of the substrate, cells/m <sup>2</sup>
$c_{p,g}$	specific heat capacity of gas, J/mol/K
$c_{p,sb}$	specific heat capacity of the substrate, J/kg/K
$c_{p,wc}$	specific heat capacity of the washcoat, J/kg/K
$D_h$	hydraulic diameter of the channel, m
$D_L$	diameter of the entire monolith brick, m
$f_{sb}$	volume fraction of the substrate in the monolith
$f_{wc}$	volume fraction of the washcoat in the monolith
$F_k$	function to specify coverages, s <sup>-1</sup>
$(\Delta H)_j$	heat of reaction for reaction $j$ (<0 for exothermic), J/mol
$h$	heat transfer coefficient between solid and gas, J/m <sup>2</sup> /s/K
$k_{m,i}$	mass transfer coefficient between solid and gas for $i$ th species, mol/m <sup>2</sup> /s
$L$	length of the monolith, m
$Nu_L$	Nusselt number for external heat loss
$R_j$	reaction rate for $j$ th reaction, mol/mol – site/s
$s_{i,j}$	stoichiometric coefficient of $i$ th species in reaction $j$
$S$	surface area of solid substrate per monolith volume, m <sup>2</sup> /m <sup>3</sup>
$S_L$	external radial surface area of converter per unit converter volume, m <sup>2</sup> /m <sup>3</sup>
$t$	time, s
$t_r$	time at which rich engine operation starts, s
$T$	temperature, K
$w$	molar flow rate of inlet gas, mol/s
$w_{sb}$	substrate thickness, m
$w_{wc}$	washcoat thickness, m
$x$	mole fraction of species
$z$	axial coordinate, m

## Greek symbols

$\Gamma_f, \Gamma_r$	time for thermal front propagation, s
$\theta$	fraction of Cerium in the oxidized state
$\theta_k$	coverage parameter or coverage fraction
$\lambda_{air}$	thermal conductivity of air, W/m/K
$\lambda_{sb}$	thermal conductivity of the substrate, W/m/K
$\rho_{sb}$	substrate density, kg/m <sup>3</sup>
$\rho_{wc}$	washcoat density, kg/m <sup>3</sup>
$\tau_f$	time required for the thermal front to travel the entire front brick, s
$\tau_r$	time required for the thermal front to travel the entire rear brick, s

## Subscripts and superscripts

$a$	ambient
$g$	gas phase
$i$	$i$ th species
$in$	inlet
$init$	initial
$j$	$j$ th reaction
$s$	solid phase
$sb$	substrate

the thermal stability decreases in the order of Rh > Pt  $\gg$  Pd while the thermal stability ranking changes to Pd  $\gg$  Rh > Pt (Bartholomew, 2001; Fiedorow et al., 1978; Shinjoh et al., 1991) in oxidizing environment. Shinjoh et al. (1991) showed that the relative sintering rates of the noble metals supported on Al<sub>2</sub>O<sub>3</sub> correlate well with the vapor pressures of the surface species (metals or oxides) present on the catalyst during thermal aging. This explains why all the noble metals (particularly Pt and Rh), with the exception of Pd, sinter more rapidly in oxidizing atmosphere than in reducing or neutral atmosphere. One important additional contributor to catalyst deactivation under high-temperature lean conditions is harmful Rh–Al<sub>2</sub>O<sub>3</sub> interaction, which leads to a significant decrease in the accessible surface Rh as a result of diffusion of the Rh ion (Rh<sup>+3</sup>) into the bulk of the alumina (Wong and McCabe, 1989; Yao et al., 1980) or formation of difficult-to-reduce Rh suboxides (e.g., RhO) (Beck et al., 1993).

Consistent with these literature findings, high-temperature lean (oxidizing) aging is found to be particularly detrimental to three-way catalyst (TWC) performance, especially for Pt or Rh-containing catalytic converters (Carol et al., 1989; Hammerle and Wu, 1984; Stenbom et al., 1990). In reducing or neutral atmosphere, on the other hand, TWC performance remains nearly unaffected after aging at temperatures up to 1050 °C (Carol et al., 1989; Hammerle and Wu, 1984). Such a strong sensitivity of catalyst deactivation to the stoichiometry of the gaseous environment during high-temperature exposure has important implications in the design and operation of automotive exhaust catalysts. For example, a fuel cut-off strategy on deceleration and lean combustion are expected to be implemented to a greater extent in future vehicles for improved fuel economy. This can potentially expose TWCs to lean exhaust at high temperatures during vehicle use, causing severe catalyst performance degradation, and thus it is critically important to develop TWCs capable of withstanding exposure to high-temperature lean conditions.

Since evaluating the long-term durability of automotive catalysts is costly and time-consuming, various rapid catalyst aging cycles have been developed to simulate the deterioration of catalyst performance under real-world driving conditions, with a goal to achieve the equivalent catalyst deactivation in a reduced time (Heck et al., 1992; Kumar et al., 1994; Skowron et al., 1989). One class of accelerated catalyst aging methods used extensively by General Motors and catalyst suppliers is engine-based exothermal aging cycles (Hughes et al., 2003; Kumar et al., 1994) (referred to as “GMAC cycles”). In this aging method, the catalyst in the converter housing is subjected to a high-temperature exhaust gas stream from an engine-dynamometer set-up, which is operated following a prescribed sequence of operating conditions to provide the specified exhaust temperature and air-fuel ratio (A/F) during the one-minute cycle. The aging cycle begins with stoichiometric operation of the engine followed by open-loop fuel-rich operation before returning to closed-loop stoichiometric control, with supplemental air injected upstream of the converter during part of the fuel-rich engine operation to raise the catalyst bed temperature by reaction exotherm. The amount of air injected is adjusted to provide lean exhaust at the converter inlet, thereby exposing the catalyst to high-temperature lean conditions. This one-minute cycle is repeated for the total aging time desired.

There are several different GMAC aging cycles depending on the catalyst-inlet gas temperature level and the length of

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