



## Experimental and modeling study of selective ammonia oxidation on multi-functional washcoated monolith catalysts



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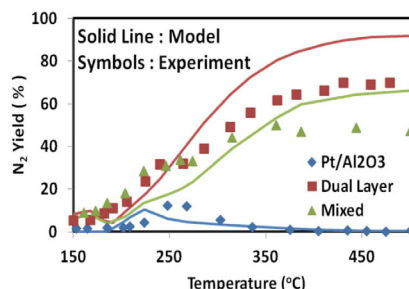
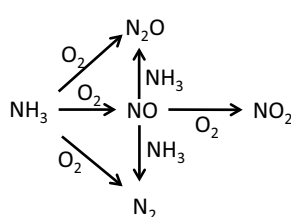
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### HIGHLIGHTS

- Mixed and dual-layer monoliths were compared at various feed compositions.
- Mixed catalyst performs better at low temperature (150–300 °C) with lower N<sub>2</sub>O yield.
- Dual layer catalyst performs better at T > 300 °C giving lower NO<sub>x</sub> yield.
- 1+1 D monolith model combine reaction kinetics on Pt catalyst and Fe-ZSM-5 catalyst.
- Model confirms the experimentally observed NH<sub>3</sub> conversion and product selectivity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

An experimental and modeling study of the selective oxidation of ammonia to N<sub>2</sub> on washcoated multi-functional Pt/Al<sub>2</sub>O<sub>3</sub> + Fe-ZSM-5 monolith catalysts is reported. The catalysts are compared for a range of temperature, space velocity, and feed composition in the presence of H<sub>2</sub>O and CO<sub>2</sub>. The addition of the Fe-ZSM-5 is effective in converting the NO<sub>x</sub> produced by the poorly selective Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. In the absence of feed NO, the dual-layer catalyst has a high selectivity to N<sub>2</sub> due to selective reaction in the Fe-zeolite layer between NH<sub>3</sub> from the bulk and counter-diffusing NO<sub>x</sub> formed in the underlying Pt/Al<sub>2</sub>O<sub>3</sub>. For T < 300 °C the mixed Fe-ZSM-5/Pt/Al<sub>2</sub>O<sub>3</sub> catalyst has a lower N<sub>2</sub>O yield than the dual-layer Fe-ZSM-5/Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. This is attributed to NO migration and reduction on the Fe-ZSM-5. The mixed washcoat gives a lower N<sub>2</sub> yield than the dual-layer due to Pt-catalyzed NH<sub>3</sub> oxidation to NO<sub>x</sub>, which diffuses to the gas phase before its reduction. The mixed catalyst is less selective to N<sub>2</sub> because the Pt catalyst in proximity to the SCR catalyst leads to the oxidation of NH<sub>3</sub> back to NO<sub>x</sub>. Most of the trends are predicted by a 1+1 D reactor model that includes the Pt/Al<sub>2</sub>O<sub>3</sub> ammonia oxidation and Fe-ZSM-5 SCR kinetics and the relevant transport processes. Kinetic parameters are estimated from single catalytic component experiments while the effective diffusivities in the layers are estimated from the simulation of multi-layer experiments in which inert top layers of γ-Al<sub>2</sub>O<sub>3</sub> and Na-ZSM-5 were deposited onto an underlying Pt/Al<sub>2</sub>O<sub>3</sub> layer. With the help of the model, explanations of the trends are provided.

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### 1. Introduction

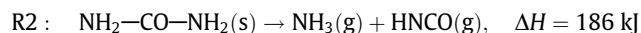
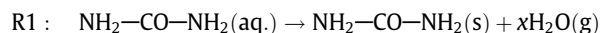
Diesel and lean burn engines are gaining popularity due to their higher fuel economy and lower greenhouse gas emissions compared to gasoline engines. However, diesel engines are required

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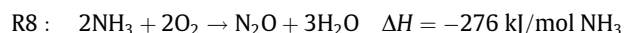
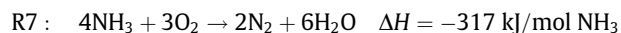
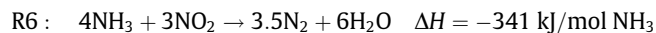
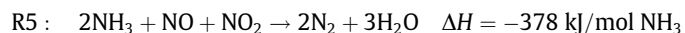
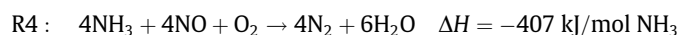
### Nomenclature

$a$	width of the monolith channel (m)	$\langle u \rangle$	average fluid velocity in the fluid phase (m/s)
$C_{pt}$	total concentration of Pt (mol/m <sup>3</sup> )	$t$	time (s)
$C_{Tm}$	total gas concentration (mol/m <sup>3</sup> )	$T$	monolith temperature (K)
$D_f$	diffusivity of species in the fluid phase (m <sup>2</sup> /s)	$x_f$	cup-mixing mole fraction in fluid phase
$D_e$	effective diffusivity of species in the washcoat (m <sup>2</sup> /s)	$x_s$	mole fraction fluid–washcoat interface
$E_{ar}$	Activation energy of reaction $r$ (J/mol)	$x_{wc}$	species mole fraction in the washcoat
$k_{me}$	external mass transfer coefficient (m/s)	$y$	length co-ordinate along radial direction (m)
$k_{or}$	pre-exponential factor of reaction $r$ (1/s or m <sup>3</sup> /mol/s)	$z$	length co-ordinate along axial direction (m)
$L$	length of the monolith (m)		
$m$	number of mesh points in radial (washcoat) direction	<i>Greek letters</i>	
$N$	number of mesh points in axial direction	$\varepsilon_{wc}$	porosity of washcoat
$P$	transverse Peclet number	$\lambda$	ratio of diffusivity of species in the fluid phase to effective diffusivity in the washcoat
$R_r$	specific reaction rate (1/s)	$\nu_{jr}$	stoichiometric coefficient of species $j$ for reaction $r$
$R_{\Omega 1}$	effective transverse diffusion length for flow area (m)	$\theta_k$	fractional surface coverage of species $k$
$R_{\Omega 2}$	effective washcoat thickness (m)	$\tau_{wc}$	tortuosity factor of the washcoat
$Sc$	Schmidt number		
$Sh_e$	external Sherwood number		

to meet current and future emission regulations of oxides of nitrogen (NO<sub>x</sub>) like Tier 2 and EURO VI [1]. One approach to comply with these stringent NO<sub>x</sub> emission regulations is through the now-commercialized selective catalytic reduction (SCR) of NO<sub>x</sub>. In most applications the reductant is NH<sub>3</sub> which is generated onboard through the following set of decomposition and hydrolysis reactions:



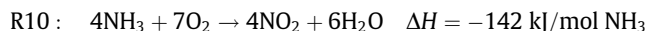
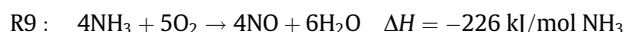
SCR technology uses metal- (Cu- or Fe-) exchanged zeolites, both of which have the requisite NH<sub>3</sub> affinity and reduction activity for NO<sub>x</sub> conversion to N<sub>2</sub>. The selective reduction of NO<sub>x</sub> to N<sub>2</sub> in presence of NH<sub>3</sub> takes place through one or more of the following reactions:



Readers are referred to [2] for the detailed description on the NH<sub>3</sub>–SCR system. The SCR system must meet emission reduction targets under the dynamic conditions of the vehicle and for this reason robust control schemes have been developed.

Conditions that are encountered in practice for which the slippage of the reductant ammonia is unavoidable include incomplete NO<sub>x</sub> conversion, release of the stored ammonia during an exhaust temperature increase, overdosing of NH<sub>3</sub>, and SCR catalyst deactivation due to aging [3,4]. An ammonia slip catalyst (ASC) is positioned downstream of the SCR catalyst, either as a short section on the same monolith “brick” or as a separate brick [5]. The function of this ASC is to oxidize ammonia directly into benign N<sub>2</sub>, global reaction R7 above. Precious group metals (PGM), particularly Pt and Rh, are effective ammonia oxidation catalysts [5–9]. However, they have poor selectivity towards desired product N<sub>2</sub> and high

selectivity towards undesired products N<sub>2</sub>O, NO and NO<sub>2</sub> [7,8,10–13] through global reactions R8 above, as well as:



The formation of NO and NO<sub>2</sub> (NO<sub>x</sub>) in the ASC is counterproductive for an aftertreatment system that is designed to minimize the emissions of NO<sub>x</sub>. Further, N<sub>2</sub>O is a 270× more potent greenhouse gas (GHG) than CO<sub>2</sub> [14] and its emission is subject to emerging GHG regulations.

There is a need to develop highly active, selective and robust ammonia slip catalysts that can tolerate the demanding diesel exhaust environment while maintaining a high activity and selectivity over a wide range of temperature, space velocity, and gas composition. The current state-of-the-art ASC uses a bi-functional catalyst containing Pt/Al<sub>2</sub>O<sub>3</sub> as the oxidative function and a Cu- or Fe-exchanged zeolite as the reductive function [5,15–17]. Recently, an ASC with a dual-layer architecture was communicated [5]. This architecture comprised a Pt/Al<sub>2</sub>O<sub>3</sub> bottom layer with a Pt loading of 10 g/ft<sup>3</sup> monolith and Cu- or Fe-exchanged zeolitic top layer. The working principle of the dual-layer design involves an intriguing counter-diffusion and reaction process. Ammonia that slips from the upstream SCR diffuses from the flowing gas to the multi-layer catalyst where it first encounters the SCR layer. Some of the NH<sub>3</sub> is stored and reacts in this layer while the remaining NH<sub>3</sub> diffuses to the underlying Pt/Al<sub>2</sub>O<sub>3</sub> layer, where it is oxidized to a mixture of N<sub>2</sub>, N<sub>2</sub>O, NO, and NO<sub>2</sub>. The NO and NO<sub>2</sub> product diffuses into the adjacent SCR layer where selective catalytic reduction by the counter-diffusing NH<sub>3</sub> occurs.

Recent studies have examined the synergies of oxidation and reduction on multi-component catalysts. Scheuer et al. [5,6,18–20] used a 2-D reactor model containing a reaction scheme with kinetics approximated by a spline interpolation of pre-computed rate data. Colombo et al. [17,21] developed the Layer + Surface Model (LSM) to simulate the dual-layer catalyst. The LSM considered the PGM layer to be a nonporous catalytic wall while the SCR top layer to be a conventional diffusion and reaction medium. Kamasamudram et al. [16] used an accelerated aging technique to study the change in ASC performance with age. In our previous study, we reported data for the dual-layer ASC comprising bottom Pt/Al<sub>2</sub>O<sub>3</sub> and top Cu–ZSM-5 layers [22]. We demonstrated the trade-off between the NH<sub>3</sub> conversion and N<sub>2</sub> selectivity due to the variation of the SCR layer loading. In a more recent study

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